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THE JOURNAL  
—OF THE—  
AMERICAN CHEMICAL SOCIETY.

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VOLUME XVIII.  
1896.

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COMMITTEE ON PAPERS AND PUBLICATIONS:

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# THE JOURNAL

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## AMERICAN CHEMICAL SOCIETY.

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### ON THE DETERMINATION OF CARBON DIOXIDE BY ABSORPTION.

BY H. HEIDENHAIN.

Received October 29, 1895.

OF all the methods for the determination of carbon dioxide the absorption method is the most reliable and most correct. It is however not easy to obtain good results with an absorption apparatus. The inexperienced generally get varying results; after some practice the results become uniform, but either always too high or too low. The application of a corresponding correction may be used with advantage in such cases, but one must admit that this is a makeshift only. As long as the causes for the excesses or shortages are unknown, the influence of such causes can not be estimated, and therefore one is always uncertain whether the applied correction actually compensates the error.

I therefore decided to seek the causes. If I could not remove them, I would at least measure their influence. The correction which was so far found by merely empirical methods could then be calculated from the obtained data. Thus the method would be brought beyond dispute, at least from the scientific standpoint.

The method and the apparatus which I shall discuss in the following are those described by Fresenius.<sup>1</sup> Before going into details, I may briefly remind the reader of them. The carbon

<sup>1</sup> Quant. Anal. I, page 449. and II, page 308.

dioxide is developed by boiling with a dilute acid. A mixture of carbon dioxide, air and water vapor is generated, from which the latter is removed first. From the remaining gas mixture carbon dioxide is absorbed. These operations are performed by a current of air free from carbon dioxide. Consequently the apparatus has to provide for

- (1) an air purifying device,
- (2) a developing apparatus,
- (3) a drying apparatus,
- (4) an absorption apparatus,
- (5) an aspirator.

Each of these parts must do its work perfectly, if good results are to be obtained. This can be easily accomplished as to the air purifying and the drying apparatus by making them amply large. The evolution flask can be rather small with substances which do not foam, but with foaming substances like baking powder the size of the flask must be chosen according to the practical requirements. For our work a capacity of 300 cc. is sufficient.

The absorption apparatus occasions some difficulty. Its size is limited by the capacity of the analytical scale. We use U tubes filled with soda-lime and calcium chloride as recommended by Fresenius. My experience is that these tubes contain generally too little calcium chloride, whereby losses are caused. Soda-lime loses some moisture in a current of air dried by calcium chloride. In order to retain the moisture a considerable length of calcium chloride must be provided at the end of the second U tube. Fresenius prepares both tubes alike and exchanges them after the first use in order to have the fresher filling in front the second time. I do not think that this is the best plan. My opinion is that each tube has to serve a particular purpose, and should consequently have a special outfit. In the first tube carbon dioxide is to be absorbed and therefore it must be filled mainly with soda-lime. The second tube has to answer two different requirements. Firstly it has to act as a safety tube to catch any residue of carbon dioxide not absorbed in the first tube. If it is considered that these traces naturally are in a highly dilute state, it seems indispensable that in order to

retain them with safety a powerful absorbent must be employed, in other words, a fresh filling. Secondly it has to absorb the moisture which during the operation has been given off by the soda-lime in both tubes. This can be attained only if the current of air passes a rather long column of calcium chloride before leaving the tube. To meet these requirements the second tube is filled half with soda-lime and half with calcium chloride.

As already mentioned, the first absorption tube receives mainly a filling of soda-lime. Only at the end at which the current of air enters a layer of calcium chloride is provided in order to absorb any moisture which may rise from the soda-lime in this direction.

This manner of filling the two absorption tubes has proved very satisfactory. Experience teaches very soon how much carbon dioxide can be absorbed by the first tube with safety and how often the filling must be renewed. We found that with our soda-lime twenty grams of filling can take up one gram of carbon dioxide. The filling of the second tube, which consists of about ten grams of soda-lime and ten grams of calcium chloride, needs renewing but seldom. As we work its weight increases at each determination very constantly by about five milligrams, whether the quantity of carbon dioxide be large or small or a blank determination be made. This proves that the small increase is caused entirely or almost entirely by moisture. When after repeated use the total increase amounts to about two-tenths gram it is observed that the increase diminishes and at the same time the results are low. Therefore we renew the filling as soon as the total increase amounts to one-tenth gram.

The aspirator is another part to which in my opinion not enough attention is paid. As will be shown later in this article, the aspirator must allow a perfect regulation of the air current and must show the quantity of air used. Both are easily attained by employing a Mariotte's bottle.

As to the manner in which the method is to be carried out, the following points seem to be worth noting. It is evident that the current of air must not exceed a certain rapidity if the absorption is to be complete in all parts of the apparatus. As the absorption of carbon dioxide by soda-lime takes place according

to general experience very easily and quickly, there is practically no danger of loss. Long columns of calcium chloride in the drying tubes secure proper absorption of moisture in this part. It remains only to make the absorption of moisture in the second weighed tube perfect. In my opinion it is impossible to give on this point any definite rules which can be followed in all cases. On the contrary the maximum rapidity admissible must be found by experiments, not only for each apparatus but also for each new lot of absorbents, as especially the commercial soda-lime has a varying content of moisture.

In order to find the allowable rapidity of the air-current one may proceed practically as follows: The apparatus is charged exactly as for an analysis except that the carbonate is left out; in other words, a blank experiment is made. The aspiration is started with a rapidity of fifty cubic centimeters per minute. After two liters of air have passed it is interrupted. If the absorption tubes show a loss in weight the experiment must be repeated with less rapidity, say forty cc. per minute, and in this manner must be continued until the weight of the tubes is constant. If the work has been done with due precaution it will now be found that the first tube has lost just as much as the second has gained. If this is not the case it is a sure indication that the result is due to a compensation of errors.

The ascertained maximum of rapidity of the air-current must not be exceeded in determinations; a slower rate is unobjectionable. It may be mentioned here that the calcium chloride in the second tube must be of the same quality as that in the drying apparatus, which is also evident from the remarks made by Fresenius.<sup>1</sup>

Further it is manifest that a certain quantity of air must be aspirated in order to transfer all carbon dioxide from the evolution flask and the drying apparatus to the absorption tubes. The common directions on this point, as for instance two air-bubbles a second for half an hour, and similar rules, are too indefinite, and in fact do not suffice. On the contrary the required quantity of air must be determined for each apparatus. This is done simply by liberating about a half gram carbon

<sup>1</sup> Quant. Anal., 1, 72.



dioxide in the evolution flask, aspirating a certain quantity of air, for instance one-half liter, weighing the tubes and repeating the aspiration until the weight of the tubes remains constant. As a precautionary measure some addition is to be made to the minimum thus found.

In order to regulate the current of air and to keep it constant some skill is required. The aspirator must not be put in operation before the air in the apparatus comes to equilibrium, which generally is the case after the liquid in the evolution flask has boiled a few minutes. The flame is then reduced just far enough to keep the liquid slightly boiling. Now the aspirator is connected and the water allowed to run off until it comes to a standstill. Now is the time to open the cock between the evolution flask and the air purifying apparatus. Immediately the outflow from the aspirator starts and becomes constant after a few seconds. By aid of watch and measuring cylinder the speed is soon regulated.

We make it a rule to aspirate with but half the allowable rapidity until the main quantity of carbon dioxide is absorbed, *i. e.*, until the soda-lime tube has recooled; from then to the end of the operation the full speed is used. It may be said that in our work these speeds are respectively ten cc. and twenty cc. per minute.

The flame remains burning during the whole time of aspiration. If the flame were extinguished the air in the evolution flask would cool and contract, making a regulation of the air-current impossible.

Another point often overlooked is the presence of carbon dioxide in distilled water and laboratory air. There is too much in both to neglect. The whole apparatus, including the evolution flask, must be filled with air free from carbon dioxide and the distilled water must be freed from it by boiling with a little acid. In pouring the water into the evolution flask air must not be allowed to enter.

Finally, corrections for changes of temperature and air-pressure are indispensable, as the tubes and their contents occupy a rather large volume.

In regard to accuracy of our results little remains to be desired. Blank determinations give a gain or loss of not more

than two-tenths mg., and determinations of carbon dioxide in clear crystals of Iceland spar give, if one gram is employed, results which vary from 44.01 to 43.96 per cent. The explanation for these slight variations may be found partly in the inexactness of the weighings, of which four must be made for every determination, and partly in the quantity of moisture condensed on the surface of the tubes, which varies according to the moisture in the surrounding air.

It may be well to append a sketch of the apparatus as modified by me. Great care has been taken to draw all parts in proper proportion. The ratio is 1 : 12.

Some explanations in regard to details may follow :

*a.* Air-purifying cylinder, filled with soda-lime. At the top is cotton to keep back soda-lime dust.

*b.* Cock to regulate the air-current.

*c.* Capillary tube to offer resistance to the air current in case cock *b* is opened too far.

*d.* Funnel tube, closed at the bottom by a perforated rubber stopper into which

*e.* a glass tube is fitted. This arrangement, in connection with cock *b*, is a substitute for a three-way cock, but has the advantage that the regulating part, *i. e.*, "*b*" does not become wet and is not exposed to heat.

*f.* Evolution flask.

*g.* Cooler. Consists of a glass tube around which a lead pipe is wound. It was adopted by us on account of varying water pressure. It stands sudden changes of pressure very well.

*h.* Drying tube filled with coarse calcium chloride.

*i.* A little pumice stone prepared with copper sulphate.

*k.* Drying tube filled with fine calcium chloride.

*l.* Cock to close drying apparatus when not in use.

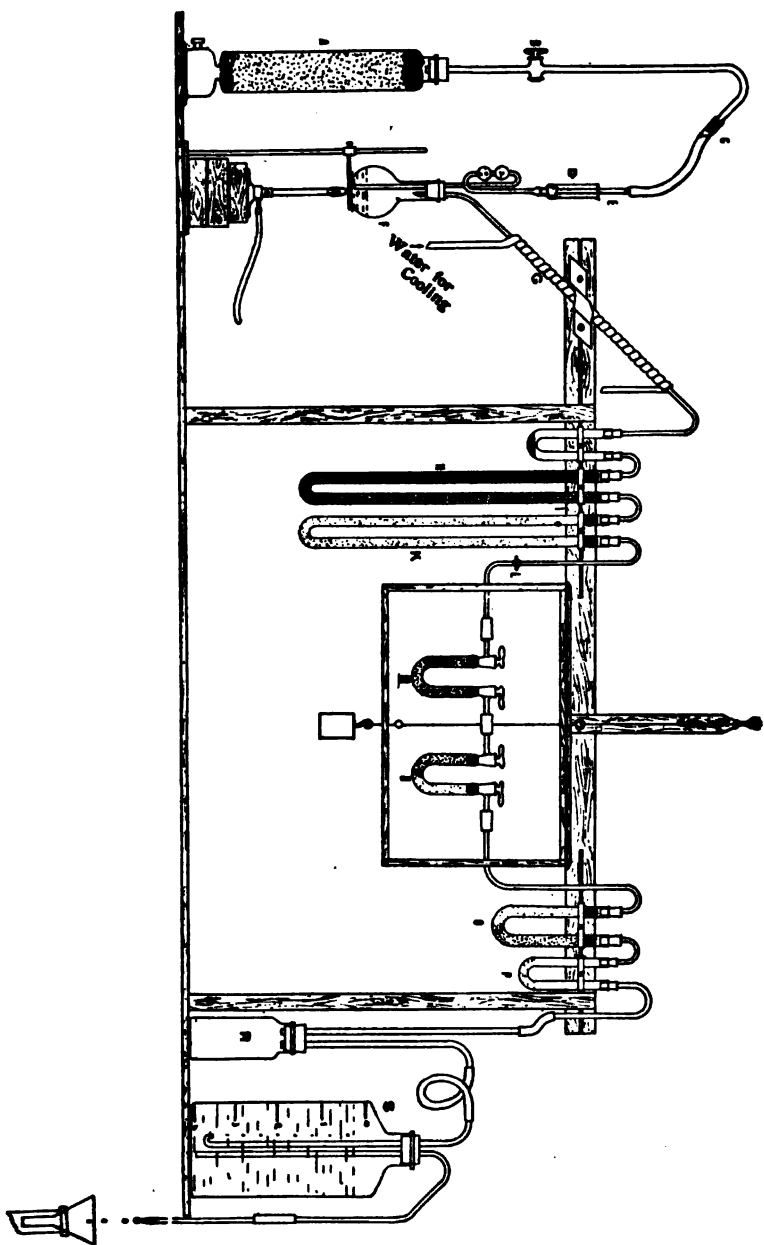
*m* and *n.* Absorption tubes, filled as described above. They are put in a glass case to protect them from dust. The connections are made by perforated rubber stoppers.

*o.* Guard tube, containing calcium chloride and soda-lime.

*p.* Indicator tube.

*r.* Safety bottle, to receive water which may be sucked back from

*s.* The aspirator.



IMPROVED APPARATUS FOR CARBON DIOXIDE.

## THE NATURAL OXYCELLULOSES.

By C. F. CROSS, E. J. BEVAN AND C. BEADLE.

Received October 10, 1895.

**I**N a previous short communication<sup>1</sup> we dealt with a controversial point which had arisen in regard to the constitution of the furfural-yielding constituents of plant-tissues. What there has been at issue between de Chalmot and ourselves in this matter, is at least clearly stated, and we have been engaged in accumulating experimental material as a further contribution to the solution of an important question in the chemistry of tissue-formation, which cannot usefully be further discussed *a priori*.

In this investigation we have been ably assisted by our friend Mr. Claude Smith, who has carried out the whole of the laboratory work, and Dr. Voelcker, the well known chemist of the Royal Agricultural Society, who has kindly cooperated with us in placing his laboratory at our disposal and supplying material for the investigation.

In the first instance we have traced the history of selected crops of barley, in relation to the elaboration of "furfurids," to use a convenient short description of these characteristic furfural-yielding constituents.

The crops selected were grown upon two of the experimental plots of the Royal Agricultural Society's station at Woburn, (England):

Plot 1 representing a soil permanently unmanured and growing barley continuously.

Plot 6<sup>2</sup> on the other hand is manured with the maximum of fertilizers and gives continuously the maximum yield of straw and grain.

These plots represent therefore the extreme conditions of growth, unfavorable and favorable.

The plants were harvested at intervals of one month and investigated according to the subjoined scheme:

(1) The "total furfural," obtained by "distilling" the entire plants with hydrochloric acid, was determined.

(2) The plants were treated for the elimination of pentosans

<sup>1</sup> This Journal, 17, 286.

<sup>2</sup> Manured with potassium, sodium and magnesium sulphates, calcium superphosphate and sodium nitrate.

and generally, of constituents not belonging to "permanent tissue," as follows:

(a) Exhaustive treatment with boiling alcohol; (b) Digestion in alkaline solution of one and one-half per cent. sodium hydroxide for some hours, followed by washing, first cold, lastly at the boiling temperature; (c) Digestion in dilute one and one-half per cent. hydrochloric acid for some hours, followed as before, by cold and hot washings. The product of these treatments may be taken as fairly representing the cellular tissue of the plant *less* the cell-contents, and may be described as permanent tissue. This description we admit is somewhat arbitrary, but it will be conceded that the residue from the treatments above described is free from pentosans and all the more readily hydrolyzable constituents of the growing plant.

It is unnecessary to reproduce minutely the experimental details of the investigation. It is sufficient to state that the results were in all cases controlled by duplicate experiments.

Date.	Age of crop.	Plot.	Total dry weight in per cent.	Furfural per cent. of dry weight. (a)	Permanent tissue per cent. of total.	Furfural from permanent tissue. Per cent.		
						tissue. (b)	original. (c)	ratio. a : c.
May 7	6 weeks	{ 1	19.4	7.0	53.4	12.7	6.8	1.03 : 1
		{ 6	14.7	7.0	55.9	12.3	5.8	1.20 : 1
June 4	10 weeks	{ 1	17.6	7.7	52.9	11.6	6.1	1.26 : 1
		{ 6	13.5	8.1	58.5	13.4	7.8	1.04 : 1
July 10	15 weeks	{ 1	42.0	9.0	65.7	9.8	6.4	1.40 : 1
		{ 6	32.9	10.6	65.7	12.5	8.2	1.30 : 1
August 21	21 weeks	{ 1	64.0	11.9	70.0	14.5	10.1	1.17 : 1
		{ 6	64.6	13.4	70.5	15.0	10.6	1.26 : 1
August 31 <sup>1</sup>	22 weeks 3 days	{ 1	84.0	12.6	75.0	16.5	12.4	1.02 : 1
		{ 6	86.4	12.4	78.4	15.1	11.8	1.05 : 1

With regard to the distribution of the furfuroids in the plant the following determinations were made in specimens taken from plot 6, on July 18, the crop being sixteen weeks old :

	Whole plant (moist). Per cent.	Whole plant (dry). Per cent.
Stems .....	50.0	41.7
Leaves .....	15.3	19.6
Ears .....	34.6	38.6

<sup>1</sup> The samples taken on August 31st were *after* the crops were harvested.

	Dry matter. Per cent.	Ash, dry matter. Per cent.	Permanent tissue. Per cent.	Furfural gross.	Furfural in permanent tissue.
Stems .....	32.6	4.0	76.6	9.5	12.2
Leaves .....	50.1	7.0	49.7	12.1	16.0
Ears.....	44.2	7.0	79.0	7.5	9.6

It appears from these results that the leaves contain a large proportion of the easily hydrolyzable furfuroids, *e. g.*, pentosans; those of the stems and ears, on the other hand, are for the most part in the more resistant form of tissue-furfuroids. The higher proportion of furfuroids in the leaves may be taken as correlated with the special assimilating functions and more active oxidizing conditions obtaining in these organs, and as indicating that furfuroids of lower molecular weight may be assimilated or elaborated to permanent tissue. The probability of this must in fact be admitted. For although de Chalmot's experiments<sup>1</sup> contradict the hypothesis that the pentoses are so elaborated, the problem as regards oxidized hexose derivatives can hardly be considered as having been seriously attacked.

The investigations of these barley plots are being continued during the current year, with special attention to the more positive indications of the above results. The following are the results of the examination of specimens taken on May 15, the crop being seven weeks old; the figures represent percentages:

	Plot 1.	Plot 6.
Total dry matter.....	20.6	17.8
Ash of dry matter.....	13.7	18.0
Nitrogen of dry matter.....	3.65	3.87
Alcoholic extract .....	19.0	23.8
Nitrogen of alcoholic extract.....	2.5	2.8
Permanent tissue .....	53.9	56.7
Ash of permanent tissue .....	3.8	4.0
Nitrogen of permanent tissue.....	4.2	4.5

The furfural numbers calculated on the dry ash-free products are as follows:

	Furfural in permanent tissue.			
	Furfural gross. Per cent.	Per cent. of tissue.	Per cent. of original.	Ratio.
	(a)	(b)	(c)	a : c
Plot 1.....	7.6	10.6	5.50	1.40 : 1
Plot 6.....	7.1	10.0	5.44	1.12 : 1

<sup>1</sup> This Journal, 16, 618.

These numbers confirm those of the 1894 crops in their general bearings. The season, however, has been so far very different, the week preceding the 15th being cloudless with high summer temperature, as against a cold wet week in the corresponding period of 1894. The higher ratio  $a : c$  accords with the higher rate of assimilation obtaining under such conditions.

The more extensive scale of the investigation has reference to a more strictly physiological scheme of observation to be made at the critical period of growth, *vis.*, flowering, fruiting, and ripening of the grain. These numbers lead to the following conclusions:

1. The "permanent tissue" (cellulose) of the cereals contains *ab initio*, a large proportion of oxidized groups, *i. e.*, oxy-celluloses.

2. The furfuroids of the cereals (Haulm) are localized mainly in the cell-substance, in the earlier and later stages of growth, in fact, almost exclusively. Towards the period of most active growth the proportion of tissue furfuroids falls from ninety to seventy-five per cent. of the total.

3. Increasing again during the period of maturation indicates that the furfuroids of what may be termed the lower grade are assimilated to the more resistant, or cellulose, form.

4. Extreme variations of the soil-conditions, *i. e.*, supply of inorganic nutrient material—is without effect upon the permanent tissue in the earlier and later stages of growth, but determines some variations of the proportion of tissue furfuroids in the intermediate stages.

5. The results show that the composition of the permanent tissue is a constant of the plant, and largely independent of the particular conditions of cultivation. This latter result is confirmed by the result of a similar investigation of barley straws from the Rothamsted Experimental Station. Specimens of the fully matured straws grown upon plots selected as showing extreme variations of the conditions of cultivation, gave the following results:

	Plot.	Total furfural per cent.	Permanent tissue per cent.	Furfural in permanent tissue of tissue.	per cent. of straw.
Minimum fertilization.	1.O	14.5	72.4	15.8	11.4
	3.O	15.5	72.4	14.7	10.6
	6.	15.8	72.6	15.8	11.5
Maximum fertilization	4 A.A.S.	12.4	76.4	16.2	12.4
	4 A.A.	15.1	80.2	16.0	12.8
	7.	15.0	82.3	14.1	11.6

The following are the conditions of fertilization :

Plots 1.O. and 6., were unmanured continuously.

Plot 3.O., manured with sodium, potassium, and magnesium sulphates.

Plot 4 A.A.S., manured with sodium nitrate, sodium silicate, calcium superphosphate and sodium, potassium, and magnesium sulphates.

Plot 7., fourteen tons farm-yard manure.

Plot 4 A.A., potassium, sodium, and magnesium sulphate, calcium superphosphate, and sodium nitrate.

These results are from an agricultural point of view of negative value. It was *a priori* possible that the composition of the permanent tissue would have varied with the prevailing conditions of assimilation. Such variations are not discoverable in the furfural-constants of the products, which express their most characteristic constitutional features. Physiologically, on the other hand, the results are of more positive bearing on the processes of assimilation, showing that these are in an important sense invariable.

It might be assumed in a superficial view that this conclusion was obvious *a priori*, and the experimental verification therefore gratuitous. On reflection, however, it will be conceded : (1) that we have not long been in possession of quantitative methods of diagnosing the constitutional features of the components of plant tissues—celluloses, oxycelluloses, lignocelluloses, etc.,—and (2) that, whatever the probability, the point is not specifically dealt with in works in plant-physiology,<sup>1</sup>

It is a point which we have dealt with before in regard to the typical lignocellulose, the jute fiber. In an investigation of the

<sup>1</sup> The current views on the subject of lignification and thickening of cell walls, imply that the permanent tissue in its earliest phases invariably consists of a pure (normal) cellulose. The chemist has to remember that the morphologist attaches no specialized significance to the term cellulose.



growth of the plant under the artificial conditions of "hot-house cultivation," Mr. A. Pears obtained the bast fiber, showing considerable divergence on ultimate analysis (C:H:O) from the normal Indian product, but with identical constitutional features. The low carbon percentage of the product was shown to be due to "dilution" by water of hydration; dehydration had not proceeded as far as obtained under the normal conditions of growth; but in all essential respects the quantitative chemical features of lignification were unaffected.<sup>1</sup> The point is therefore established in regard to two main types of tissue-formation.

Reverting now to the history of tissue-formation in barley plant.

In reference to the germination process, we commenced observations<sup>2</sup> upon the earliest stages of tissue-formation in regard to the formation and fixation of furfuroids, but, recognizing the prior claims of de Chalmot in this field of investigation, we are satisfied to leave the subject in such good hands, merely noting that we have joined issue with him in regard to the interpretation of the furfural-constants.

De Chalmot has especially investigated the influence of the two factors which might be expected to affect the formation and elaboration of these furfuroids, *viz.*, (1) light; (2) the supply of nitrogen (nitrate). Light was found to be without effect in these earlier stages of growth; and with a liberal supply of nitrates the amount of furfuroids in the young plants was found not to decrease. These results again point to the invariable habit of the cell in regard to the formation of tissue.

We have endeavored to produce a still more drastic variation of the conditions of assimilation, as follows: Young plants of oats seven weeks old were placed in the following solutions: (a) water; (b) dilute nitric acid of 0.25 per cent.; (c) of one-half per cent.; (d) of one per cent. The plants withered only gradually. After about ten days they were removed, dried and investigated. The results are given below:

Twenty plants before experiment weighed 25.8 grams and contained 16.7 per cent. dry matter.

Twenty plants in water (a) weighed 39.0 grams and contained 10.2 per cent. dry matter.

<sup>1</sup> *J. Chem. Soc.*, 1893, 967; Cross & Bevan: "Cellulose," pages 111-113.

<sup>2</sup> *Ber. d. chem. Ges.*, 27, 1061.

Twenty plants in dilute acid (*b*) weighed 18.0 grams and contained 21.3 per cent. dry matter.

Twenty plants in dilute acid (*c*) weighed 15.0 grams and contained 24.4 per cent. dry matter.

Twenty plants in dilute acid (*d*) weighed 13.0 grams and contained 31.0 per cent. dry matter.

From the dry matter the following percentages of furfural were obtained:

( <i>a</i> )	( <i>b</i> )	( <i>c</i> )	( <i>d</i> )
8.2	9.2	8.2	8.5

The uniformity of these numbers is curiously at variance with the extreme variations of the conditions of retrograde development, which are apparent from the statistics of the relative weights of these plants.

In a second series of experiments very different results were obtained. In this case the plants were taken at a more advanced stage of growth—thirteen weeks old. They were placed in water and dilute solutions of nitric acid, respectively, as before, remaining for ten days, when they showed signs of withering. They were removed, dried and analyzed for "total furfural," with the following results:

	Cultivations in water per cent.	Dilute nitric acid. per cent.		
		0.25	0.50	1.00
Furfural .....	4.6	4.9	5.9	7.8

These variations determined by artificial treatment may appear out of harmony with the invariability of the results obtained in the first series. It will be noted, however, that the oats show a very different initial proportion of furfuroids, and appear to contain carbohydrates susceptible of attack by nitric acid.

The more advanced period of growth (thirteen weeks) at which the plants were taken, has been previously shown to be one of maximum normal variation of the furfuroids, which is consistent with maximum variations under retrograde development, and we may in future experiments follow the indications of these observations, that the most active period of growth offers the most favorable conditions for the study of variations artificially determined.

The purpose of the present investigations being to accumulate

experimental material, the observations were extended to products of widely different origin, life-history, or formation. Subjoined are the numbers obtained with (a) mangels, and (b) gooseberries:

(a) Long red mangels were taken at intervals from a selected field, and the furfural and other constants determined, as follows :

Date.	Average wt. per root	Dry matter per cent.	Ash of dry matter per cent.	Permanent tissue per cent.	Furfural whole root (dry) per cent.	Per- manent tissue (dry) per cent.
June 30	1.5	12.7	11.0	25.3	4.1	12.6
August 6	300.0	11.5	12.0	28.8	4.3	11.4
October 11	1456.0	13.1	7.8	14.9	3.7	11.4

The furfural numbers, it will be remarked, are uniform over the whole period of growth. The proportion of furfuroids moreover is small, and further investigation of this group of products from our present point of view is therefore abandoned.

(b) The berries were examined at an interval of one month, with the following results :

Date.	Dry matter per cent.	Permanent tissue per cent.	whole fruit per cent.	Furfural permanent tissue per cent.
May 16	9.2	21.5	4.8	7.8
June 17	9.1	23.5	3.9	7.2

These numbers again are devoid of any characteristics such as invite further investigation. Other typical products were also examined with similar results. So far, therefore, the selection of the cereals as the typical case of the elaboration of cellulose-tissue with a maximum of furfuroid constituents is justified.

As we have before indicated it is not the purpose of the present communication to attempt any final conclusions as to the bearings of these results upon the general questions of assimilation and metabolism. We may perhaps again insist on the one prominent result of these investigations, which is to establish the uniform characteristics and uniform distribution of the furfuroids of the cereal straw throughout its substance:

(1) The entire straw in the matured state is characterized by yielding twelve to fifteen per cent. furfural ; and (2) the "cellulose" isolated from the straw by the severe handling of the paper-maker ; viz., digestion with caustic lye (two to three per

cent. sodium hydroxide) at elevated temperatures (forty to sixty pounds steam pressure), is identically characterized, yielding twelve to fifteen per cent. furfural on boiling with condensing acids.

This uniformity of distribution and uniformity of resistance to alkaline hydrolytic treatment of the widest range, establishes the molecular homogeneity of the tissue-substance in regard to the relative proportion of furfuroids to normal hexose groups. The results of our investigations of the history of the formation of the tissue are strictly correlative, and the elaboration of products of such characteristics must be regarded as an essential and primary property of the unit cell in the same sense that alcoholic fermentation is a property of the yeast cell. To put it perhaps more directly: the constitution of assimilated material in the plant is immediately determined by the molecular configuration of the assimilating material. This view has been expressly formulated by E. Fischer<sup>1</sup> in reference to the origin of the carbohydrates in the plant. The more evidence we have that the assimilating process remains invariable in its products, notwithstanding wide variations in the external conditions, the more necessary does it become to regard the essential *directive* factors of the process as material, *i. e.*, as residing in the material configuration of the cell rather than determined by external forces. The results of our investigations contribute to the establishment of this view.

## PART II.

### I. THE CONSTITUTION OF THE CEREAL CELLULOSES.

We have made some progress in the isolation of the "furfuroid" constituents of celluloses. The more important differences which they exhibit from the normal celluloses we have dealt with in previous papers.<sup>2</sup> Although they are not resolved by alkaline hydrolysis we have found certain reagents which determine a satisfactorily sharp separation of their furfural-yielding component groups. Thus:

(a) Pure bleached straw-cellulose was treated with sulphuric acid at 1.62 specific gravity; the cellulose dissolves to a nearly

<sup>1</sup> *Ber. d. chem. Ges.*, 27, 3231.

<sup>2</sup> *Ber. d. chem. Ges.*, 27, 1061; C. Smith, *J. Chem. Soc.*, 65, 473.

colorless solution. After standing some time (three hours from the start) the solution was poured into water. The white gelatinous precipitate of cellulose (hydrate) was filtered off and exhaustively washed, dried, and weighed. It amounted to sixty-four per cent. of the original. The reprecipitated cellulose and the filtrate were both distilled for elimination of furfural; the proportions obtained, calculated on the original cellulose, were:

	Furfural. Per cent.
Reprecipitated cellulose.....	0.6
Products soluble on dilution .....	14.0

The "furfuroids" therefore are hydrolyzed to soluble derivatives by the process.

(b) A second specimen was dissolved by heating with a concentrated solution of zinc chloride, the viscous solution poured into water, and the precipitate filtered off. Similar determinations were made as in (a), with the following results:

	Furfural (calculated on original cellulose). Per cent.
Reprecipitated cellulose.....	0.9
Product soluble on dilution.....	10.4

It is to be noted that furfural is freely formed in the process of heating with the concentrated solution of zinc chloride, and some quantity is volatilized. The reprecipitated cellulose (hydrate) has the characteristic of the normal celluloses. On combustion of these products the subjoined numbers were obtained:

Carbon .....	43.00	43.07
Hydrogen .....	7.14	6.99

corresponding with the formula  $3C_6H_{10}O_5 \cdot H_2O$ .

The products in solution in the acid liquid would appear to be capable of isolation by simple means, *viz.*, by neutralizing with barium carbonate, filtering, and evaporating.

Being derivatives of unknown constitution it was deemed advisable to prepare them in large quantity, and we proceeded to carry out the above process of hydrolysis on the scale of 100 grams per operation, as preliminary to working on the still larger scale of kilograms.

Proceeding as described we have obtained, on evaporating the filtrate from the barium sulphate, a light-colored gum resembling dextrin.

The first preparation gave, on distillation with hydrochloric acid, only eight and two-tenth per cent. of its weight of furfural; whereas, had we succeeded in obtaining the furfuroids only, as in the experiments on the smaller scale, the products should have yielded forty to fifty per cent.<sup>1</sup>

On reverting to the small scale we obtained this result :

Two grams of the cellulose being dissolved and the solution diluted and filtered from the reprecipitated cellulose ; the filtrate was boiled with barium carbonate, filtered, and made up to 200 cc. Of this solution, eighty cc. on evaporation gave 0.144 gram organic solids ; a second, eighty cc., distilled for furfural, gave an amount corresponding to 46.6 per cent. of the weight of the organic solids.

On further investigation of the products obtained on the large scale we found a large proportion retained as an insoluble barium compound. On boiling the washed precipitate with ammonia it yielded an extract, which on drying and "distilling" with hydrochloric acid, gave 12.5 per cent. furfural. It appears, therefore, that the products are resolved into three groups :

1. Normal cellulose (hydrate) reprecipitated, on dilution.
2. Soluble in water, but combining with barium carbonate to form insoluble compounds.
3. Soluble in water, but neutral, in properties, and therefore forming no barium compounds.

It appears also that the discrepancies between the results on the small and on the large scale are due to the conditions affecting group 2. These conditions are being carefully studied with the view of controlling the operation on the large scale. We have further characterized the soluble products of the hydrolysis as obtained on the small scale under most favorable conditions, as follows :

(a) *Copper-oxide reduction*.—As first obtained in solution the reduction equivalent, referred to that of dextrose as 100, has been

<sup>1</sup> Unless we assume that the configuration of the products is changed by the process of solution in sulphuric acid, which is not an improbable hypothesis. See *J. Chem. Soc.*, 65, 477.

determined at 30.6. After further hydrolyzing by boiling in the solution diluted to contain two per cent. sulphuric acid, it reached a maximum at 68.3.

(b) *Osazone*.—After hydrolysis to this maximum the products were treated with phenylhydrazine under the usual conditions of formation of osazones. A characteristic product was obtained crystallizing well from solution in benzene. It was found to melt at 154°. On analysis it gave a quantity of ammonia corresponding to eight and four-tenths per cent. nitrogen. The parent substance is still, therefore, a product of relatively high molecular weight, approximately of the dimensions  $C_{10}$  to  $C_{12}$ , or, more strictly, containing one reactive CO group in the unit of these dimensions.

(c) *Decomposition by oxidants*.—On treatment with potassium permanganate in neutral solution it gives large yields of acetic acid. The products of oxidation by Fehling's solution also contain a large proportion of this acid.

(d) *Acetylation*.—The two products of hydrolysis not yet having been isolated on the large scale, the reaction with acetic anhydride has been studied with the parent substance. These celluloses contain reactive hydroxyl groups, forming an acetate on digestion with the anhydride at its boiling-point. The yield obtained in one experiment was 124 per cent. The product being insoluble in and unaffected by the usual solvents of the cellulose acetates, it was possible that a more complicated reaction had resulted, *e. g.*, condensation of the furfuroids to furfural and union with the anhydride to furfuracrylic acid. On distillation with hydrochloric acid the product yielded nine and a half per cent. furfural, which amounts to twelve per cent. of the original cellulose. The reaction will be further investigated with the isolated furfuroids.

(e) *Qualitative Reactions*.—The cereal-celluloses, as we have frequently stated, do not give the reactions characteristic of the pentosans, nor do the soluble products of acid hydrolysis obtained as described.

The celluloses on the other hand give a rose-red coloration on boiling with solutions of aniline salts, and the reaction is also obtained with the products of hydrolysis. From the behavior

of the products with barium carbonate it appears we are dealing with two groups: a neutral group presumably aldoses, and a more acid group giving insoluble barium compounds, both characterized by the furfural reactions. The lines are obviously indicated upon which the separation and isolation of these two groups must proceed.

## II. THE CONSTITUTION OF THE CEREAL STRAWS.

The straws are obviously complex structures and therefore not chemically homogeneous. They contain a considerable proportion of lignocellulose, the lignification being most marked in the groups of thickened polygonal cells situated in the hypodermal region, and evidently contributing chiefly to the rigidity of the stem.

The following constants have been determined, certain of which may be taken as measuring the proportion of lignocellulose in the complex :

	Wheat straw.	Barley straw.
Cellulose, (chlorination method).....	45.2	45.3
Chlorination, chlorine combining.....	2.5	2.5
"    chlorine as hydrochloric acid..	2.9	2.4
Methoxyl, (O.CH <sub>3</sub> ).....	3.1	2.1
Furfural.....	14.15	14.15
Volatile acid, chiefly acetic, distilled with thirty-three per cent. sulphuric acid .....	6.4	6.3

The chlorination numbers correspond with a proportion of lignocelluloses amounting to thirty-three per cent. Of the cellulose isolated by the method of chlorination approximately one-half is obtained from this group, one-half being derived from the residual complex. The lignocelluloses giving seven to eight per cent. furfural, yield say two and six-tenths of the total fourteen and five-tenths of the straw.

The "residual" complex is therefore richer in furfuroids and has a correspondingly lower proportion of the resistant celluloses.

It may be further resolved as follows :

		Yielding furfural of cellulose. of straw. percent. percent.
Resistant "cellulose" .....	25.0	12.0
Pentosans	42.0	3.0
Hemicelluloses }		9.0

<sup>1</sup> Vide the author's book : "Cellulose," pp. 111-113.



Assuming that of the latter group of easily hydrolyzable constituents the furfural-yielding bodies are exclusively pentosans, this would amount to one-half, and the entire straw (structural elements) might be expressed in terms of its proximate constituents, as follows :

Disposition in stem.		Contain- ing cel- lulose.	Yield- ing fur- fural.
Hypodermal fibers and fibers of fibrovascular bundles.	Lignocelluloses ...	33.0 25.0	2.6
Vessels of fibrovascular bundles parenchyma and cortex.	Resistant cellulose. ...	25.0 2.50	2.6
	Hemicelluloses ...	21.0 ...	..
	Pentosans .....	21.0 ...	9.0
		100.00	14.6

It will be an object of our future investigations further to differentiate this complex.

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## NOTES UPON THE DETERMINATION OF NITRITES IN POTABLE WATER.

BY AUGUSTUS H. GILL AND H. A. RICHARDSON.

Received October 29, 1895.

IN comparing the results obtained by Trommsdorff's iodo-zinc starch method and Griess'  $\alpha$ -naphthylamine test upon a large variety of waters, discrepancies were noticed which were very marked in the case of the peaty waters. These showed no blue by Trommsdorff's method, but in some cases as high as 0.0010 parts nitrogen as  $N_2O$ , per 100,000 by the Griess test. Upon decolorizing the waters the results agreed, showing that the peaty matter interferes with the formation of the iodide of starch, and unless nitrites are present in considerable quantity (above 0.0020 parts nitrogen as  $N_2O$ , per 100,000) this test is not capable of detecting them.

The decolorization was affected in the cold, as heating increases the nitrites, by shaking up about 250 cc. of the water with three cc. of "milk of alumina,"<sup>1</sup> allowing to settle, and filtering through a filter which is washed free from nitrites. Even when using Griess' method it was found advantageous to decolorize the peaty waters, as their brown color modifies the pink tint, giving a slightly higher reading than would otherwise be obtained.

<sup>1</sup> Prepared by precipitating a boiling solution of 125 grams potash alum per liter with ammonia, allowing the aluminum hydroxide to settle and washing by decantation.

COMPARISON OF METHODS FOR QUANTITATIVE ESTIMATION OF NITRITES.

Parts Nitrogen as $N_2O_3$ in 100,000.							
		0.0000	0.0001	0.0005	0.0010	0.0015	0.0020
Decolorized tap water.	Naphtylamine .....	Mere trace of color.	The gradation was excellent and the color fully developed in twenty minutes, the highest standard developed immediately.				
	Iodo-zinc starch.....	Not a trace of blue.	The color did not fully develop until the expiration of five hours, although there was a faint color in the higher standards in an hour.				
	m-Phenyl diamine.....	Not a trace of color in any of the standards.					
Tap water (Cochituate).	Naphtylamine .....	Some color, i. e., in nitrates in Cochituate.	Excellent gradation, color developed in twenty minutes, but the color was modified by the coloring matter in the water, thus being difficult to read.				
	Iodo-zinc starch.....	Did not develop.	Did not develop.	Did not develop.	Developed in eighteen hours.	Developed in eighteen hours.	Developed in eighteen hours.
	m-Phenyl diamine.....	No increase in color over that originally in Cochituate water.					
	Water free from ammonia.	Naphtylamine .....	The gradation was excellent and the color fully developed in twenty minutes. The reading of the Cochituate to which no nitrates had been added was 0.0004.				
Iodo-zinc starch.....		The color did not fully develop until the expiration of five hours, but at the end of that time there was color in all the tubes, even the very lowest.					
m-Phenyl diamine .....		Not a trace of color in any of these standards.					

The table on the preceding page shows the effect of the peaty matter and also a comparison of the methods, together with that of the *m*-phenylene diamine.

In some cases a pink color was obtained and no blue, due probably to the greater delicacy of the naphthylamine test, it being competent to detect 0.0001 part of nitrogen as  $N_2O_5$  in 100,000. This we think is the extreme limit of the test, as different *shades*, not *depths* of color are obtained upon adding different quantities of the reagents, as Dr. J. T. Tanner<sup>1</sup> found. The iodo-zinc starch method is incapable of detecting less than 0.0002 part of nitrogen as  $N_2O_5$  per 100,000.

In a few cases a blue color appeared, but no pink, but upon passing carbon dioxide through the water no blue was obtained. This may possibly have been due to hydrogen peroxide. Where large quantities of nitrites are present, a purple color instead of a blue is obtained, which is difficult to estimate; in such cases the water should be diluted before applying the test.

In conducting the Griess test, the directions given by Dr. Tanner<sup>2</sup> were followed with the additional precaution of using water free from nitrites in the preparation of the reagents. This was prepared by distilling the middle portion of ordinary distilled water with an excess of alkaline permanganate, collecting the middle portion of the distillate thus obtained. Water prepared in this way gives no test upon eighteen hours' standing, even when tightly stoppered.

### A GRAVIMETRIC METHOD OF ESTIMATING PHOSPHORIC ACID AS AMMONIUM PHOSPHOMOLYBDATE.<sup>3</sup>

BY THOMAS S. GLADDING.

Received November 11, 1895.

THE estimation of phosphoric acid by weighing the yellow precipitate of ammonium phosphomolybdate has often been attempted, but, except in iron analysis, where the amount of phosphorus is very small, such a method has never yet been successful. The reason of such failure is evident when we consider the analyses that have been made of the yellow precipitate. A few only need be presented.

<sup>1</sup> Report National Board of Health, 1882, 280.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Read before the New York Section of the American Chemical Society, Nov. 8, 1895.

	Rammels- berg.	Struve and Svanberg.	Sonnen- schein.	Gibbs.
H <sub>2</sub> O.....	5.77	9.49	11.23	3.94
NH <sub>4</sub> OH .....	3.25	9.49	11.23	3.35
P <sub>2</sub> O <sub>5</sub> .....	3.90	3.63	3.03	3.66
MoO <sub>3</sub> .....	86.45	86.88	86.87	89.05

Gibbs gives the following formula for the salt:



He prepared the salt by mixing solutions of ammonium molybdate (seven parts of water to three of the salt) and phosphate, adding nitric acid in excess to the solution and boiling. Such a method would give more or less occluded molybdic oxide. His analyses gave 3.70 per cent. and 3.83 per cent. of phosphorus pentoxide against the theoretical percentage of 3.66. Such results were sufficiently accurate for his purposes, but would discourage any suggestion of using the yellow salt as the basis of a gravimetric method. His formula is, however, without any doubt, the correct one, with the exception of the water of crystallization.

My own analysis of the salt precipitated in the manner described later on, and dried at a temperature of 105° C. to a constant weight, gives me the following composition:

	Theoretical.	By analysis.
48MoO <sub>3</sub> .....	91.38	91.36
2P <sub>2</sub> O <sub>5</sub> .....	3.76	3.76
10NH <sub>3</sub> .....	2.25	2.31
11H <sub>2</sub> O.....	2.61	2.57

For ammonia 1.015 grams gave 0.0234 gram NH<sub>3</sub> = 2.30 per cent.

For ammonia 20.193 grams gave 0.4690 gram NH<sub>3</sub> = 2.32 per cent.

For moisture 7.25 grams gave ——— = 2.53 per cent.

“ “ 10.30 “ “ “ = 2.61 “ “

The water was determined by estimating total hydrogen by combustion with copper oxide.

For phosphoric acid, repeated analyses and syntheses gave almost exactly 3.76 per cent.

The molybdic acid was found by difference.

The fact that drying at 105° C. expels all the water except

eleven molecules, and that the yellow salt when dried over sulphuric acid in a close desiccator comes to the same weight as when dried at  $105^{\circ}\text{C}$ . would indicate that this salt contains no other water of crystallization. Any excess of water is apparently hygroscopic water and not water of crystallization. I therefore find the following as the correct formula for the crystallized yellow salt :



The following method of procedure has given me a precipitate of a very uniform composition and would seem to afford the simplest and easiest method yet presented for estimating phosphoric acid.

To the solution of phosphoric acid, (twenty-five cc. to fifty cc. in bulk, are added) twenty-five cc. of strong ammonia 0.900 sp. gr.: nitric acid, 1.42 sp. gr., is now added to acidity. The beaker containing the solution, is placed in a water-bath maintained at a constant temperature of  $50^{\circ}\text{C}$ . The ordinary ten per cent. acid molybdate solution is now added from a burette at the rate of about three drops per second, with constant stirring, (fifty cc. may be added in five minutes). When the molybdate solution to an excess of about ten cc. has been added, the beaker is allowed to remain for ten minutes in the bath. The contents are then filtered through a weighed filter paper.

The filtrate, without the washings, and after the addition of five cc. molybdate solution, is replaced in the bath for ten minutes. The liquid should remain clear or at most show only a faint opalescence.

For washing the precipitate, a wash water of dilute nitric acid 100:1 is employed. Three generous washings by decantation and three washings on the paper followed by one final washing with distilled water are sufficient. The paper and contents are now drained for a few minutes on some waste filter or blotting paper and then dried to a constant weight at a temperature of  $105^{\circ}\text{C}$ .

In this method, the formation of a pure granular precipitate of uniform composition and free from occluded salts, is secured by the gradual addition drop by drop of the molybdate solution

with constant stirring. The completeness of precipitation of the phosphoric acid is attained by the presence of a large amount of ammonium nitrate. The separation of molybdic oxide or iron salt is avoided by the low temperature employed.

For the final drying at  $105^{\circ}$  C. an air-bath was tried and decisively abandoned. The use of a liquid boiling at  $108^{\circ}$  C. to  $110^{\circ}$  C. is the only safe course. A water-oven consisting of several distinct divisions or floors, one above the other, and surrounded with dilute glycerol 1.160 sp. gr. boiling at  $110^{\circ}$  C. was found to work admirably. The lower bath or division is reserved for the final drying. None but dry or almost dry precipitates must be allowed in this lower division. The precipitate may be dried in an ordinary water-oven almost to a constant weight and then dried for one hour longer in a glycerol oven at  $105^{\circ}$  C. The filter papers used are dried at  $105^{\circ}$  C. and weighed between large, closely fitting ground watch-glasses. The final weighings of papers and contents are made in the same manner.

The following investigation serves to show the results that are secured by this method of analysis.

A chemically pure microcosmic salt was finely pulverized. Careful ignition of ten grams in a covered platinum dish gave 4.8955 grams of sodium phosphate, giving a percentage by calculation of 34.07 per cent. phosphorus pentoxide. Ten grams of the salt were now dissolved in one liter of water and aliquots taken. Twenty-five cc. containing 0.250 gram of microcosmic salt were treated exactly as above. Fifty cc. containing 0.500 gram microcosmic salt were treated by the official magnesia method. The following results were obtained :

	Taken.	Gladding method. Per cent.	Taken.	Magnesia method. Per cent.
1.....	0.250	34.07	0.500	34.07
2.....	0.250	34.08	0.500	34.05
3.....	0.250	34.06	0.500	34.09
4.....	0.250	34.10	0.500	34.08

A solution of one-tenth of the above strength was obtained by dilution. Of this the following quantities were used and the phosphoric acid therein obtained by the new method :

Taken. cc.	Yellow salt obtained.	Phosphorus pentoxide obtained.	Theoretical phosphorus pentoxide.
1 ..... 10	0.091	0.00342	0.003407
2 ..... 1	0.010	0.00037	0.00034

These last experiments demonstrate the insolubility of the yellow salt and the applicability of the new method to very small amounts of phosphoric acid.

A number of comparative tests of fertilizers gave closely agreeing results, as follows :

	Official method. per cent.	New method. per cent.
Phosphoric acid.....	28.80	28.87
" " .....	2.63	2.70
" " .....	12.03	12.00
" " .....	28.30	28.33
" " .....	15.64	15.70
" " .....	15.04	15.00
" " .....	15.19	15.23
" " .....	29.16	29.23

In all fertilizer work 0.250 gram were used for precipitation, and molybdate solution to an excess of about ten cc. was added. No more than ten cc. in excess should be used.

Tankages and fertilizers containing a notable amount of organic matter should be ignited before solution.

An application of this method to the direct determination of reverted or citrate soluble phosphoric acid promises good results. The method of procedure is as follows : The citrate filtrate and washings are made up to 200 cc. Twenty-five cc., equivalent to 0.250 gram of the fertilizer are treated as follows : Fifty cc. ammonia 0.900 sp. gr., are added and then nitric acid to acidity. The liquid is now diluted to half a liter to overcome the solvent action of the ammonium citrate, and heated in a bath to 65° C. Fifty cc. of molybdate solution are added in a thin stream with stirring and the whole digested for thirty minutes. The rest of the analysis is conducted precisely as in ordinary work, except that the filtrate is heated for thirty minutes longer at 65° C. The liquid should remain clear.

# DIPYRIDINE TRIMETHYLENE DIBROMIDE, AND A STUDY OF CERTAIN ADDITIVE REACTIONS OF ORGANIC BASES.<sup>1</sup>

BY R. F. FLINTERMANN AND A. B. PRESCOTT.

Received November 4, 1895.

IN the course of an inquiry into certain limits to the formation of the addition compounds of amines with halogen substituted hydrocarbons, an inquiry made both historically and by experimentation, the compound named first above was obtained. In this study the bases chiefly considered are the tertiary amines, and the halogen compounds chiefly those of mono- and dihalogen substitution, especially in the saturated hydrocarbons.

## ALKYL HALIDES IN THE FORMATION OF NITROGEN BASES.

Among the more simple aliphatic bases, it is obvious that there are limits (other than those of valence) to the concentration of carbon, or displacement of hydrogen, in the atomic positions next but one to the nitrogen.<sup>2</sup> Among well known products, normal propyl forms a primary, a secondary, and a tertiary amine, likewise a quaternary<sup>3</sup> base iodide, and hydroxide, the latter not decomposed at 100° C. In contrast, isopropyl has been found to form only a primary and a secondary amine. The butyls, as base-forming alkyls, behave with a like gradation of formative power. Normal butyl holds the four ammonium valencies of nitrogen.<sup>4</sup> Isobutyl, primary, forms the quaternary base iodide,<sup>5</sup> but not bromide.<sup>6</sup> Secondary butyl forms the secondary amine but sparingly, the tertiary with difficulty, and this refuses to unite with iodide of the same alkyl in formation of a quaternary base.<sup>7</sup> Finally the tertiary butyl appears to form only a primary amine, namely, trimethyl carbinamine, (CH<sub>3</sub>)<sub>3</sub>CNH.<sup>7</sup>

This was obtained by Butlerow,<sup>8</sup> as a bye-product, from tertiary butyl cyanide, during the conversion of this nitrile to tri-

<sup>1</sup> Read at the Springfield Meeting of the American Association for the Advancement of Science.

<sup>2</sup> That is, as atoms directly linked to *alpha* C.

<sup>3</sup> H. Roemer, 1873: *Ber. d. chem. Ges.*, 6, 1101.

<sup>4</sup> Lieben and Rossi, 1873: *Ann. Chem.* (Liebig), 165, 109.

<sup>5</sup> Sachtleben, 1878: *Ber. d. chem. Ges.*, 11, 733.

<sup>6</sup> Reimer, 1870: *Ber. d. chem. Ges.*, 3, 756.

<sup>7</sup> S. Reimann, 1874: *Ber. d. chem. Ges.*, 7, 1289.

<sup>8</sup> *Ann. Chem.* (Liebig), 170, 151; 162, 7, 12.



methyl acetic acid, and has been obtained, as stated, through transformation of isobutyl iodide, when acted upon by silver cyanide, by Linnemann,<sup>1</sup> and by Brauner.<sup>2</sup> Rudneff,<sup>3</sup> also has studied trimethyl carbinamine. The last named chemist found that although trimethyl carbinamine unites with tertiary butyl iodide to form the secondary base in its hydriodide,  $(\text{CH}_3)_3\text{C}_2\text{NH}\cdot\text{HI}$ ; on distilling this with potash the secondary amine was not formed, but only the primary amine again. This boils at  $45^\circ\text{C}$ . The preparation of trimethyl carbinamine by transformation of isobutyl iodide in reaction with silver cyanate, as reported by Linnemann,<sup>4</sup> was tried by A. W. Hofmann, in 1874,<sup>5</sup> without success, obtaining chiefly isobutylamine, after which Brauner, at Linnemann's request, went over the work with great care, and has reported the operation with his interpretation of the reaction and his successful production of the primary amine of the tertiary alkyl, as above cited. He obtained, however, both isobutylamine and the tertiary butylamine. In repeating his operation twice, the second time with rigid rectification of materials and products, we obtained the hydrochloride of a base which agrees in centesimals with a pure butylamine. On distilling this over potassium hydroxide, no distillate was obtained of a boiling-point below  $65^\circ\text{C}$ . The first distillate had just the boiling-point of isobutylamine, primary amine of primary alcohol, a result which only gives to us another indication that tertiary alkyls do not form amines with readiness.

The greater avidity of methyl halides than of ethyl halides, in additive reaction with tertiary bases, is a common laboratory observation. This difference, however, cannot be attributed wholly to the ratio of hydrogen carried by the carbon atom linking to nitrogen, because of the higher ratio of total hydrogen to total carbon in the methyl as compared with entire ethyl. But the disparity in reactive strength between propyl and isopropyl can be theoretically attributed to the one difference between the two alkyls, the structural difference in ratio of hydrogen to car-

<sup>1</sup> 1872: *Ann. Chem.* (Liebig), 162, 19.

<sup>2</sup> 1876: *Ann. Chem.* (Liebig), 192, 65.

<sup>3</sup> 1876: *Ber. d. chem. Ges.*, 11, 988, 1938; 12, 1023; 1880. *Bull. Soc. chim.*, [2], 33, 297.

<sup>4</sup> Already cited. This transformation agrees with that of isobutyl alcohol into trimethyl carbinol, reported at the same time by Linnemann: *Ann. Chem.* (Liebig), 162, 12.

<sup>5</sup> *Ber. d. chem. Ges.* 7, 508.

bon in positions nearest the nitrogen. In speed of additive reaction toward triethylamine, Menshutkin<sup>1</sup> found that of normal propyl iodide to be 0.0116, that of isopropyl iodide to be 0.00121, in like measures of the two. Normal butyl was to isobutyl as 0.00832 to 0.00191. Ethyl to normal propyl as 0.00584 to 0.000984, all the alkyls acting as iodides, the reactions being compared in the same solvent. In recent studies<sup>2</sup> of the same investigator, tertiary amines are compared with secondary and primary amines in speed of additive reaction with the same alkyl bromide, in each of four series. Toward methyl bromide, diethylamine is to dipropylamine, as 16886 to 10264; toward ethyl bromide, the same amines, respectively, as 182 to 101, in speed of addition. Using electrolytic measurement of the affinity coefficients, Bredig<sup>3</sup> finds the quaternary organic bases to be the strongest and the tertiary the weakest, each taken in its ammonium chloride.

The limits of the addition of aliphatic tertiary bases, those of simple composition, to halogen substituted hydrocarbons, have been lately studied by Kleine,<sup>4</sup> the chief question being the additive capacity of a secondary, and a tertiary, halogen substituted group. The bases studied were trimethylamine and triethylamine: the halides were monobromine and dibromine substituted hydrocarbons in the saturated series as far as pentane, as well as various unsaturated derivatives of open carbon chain. It was concluded by Kleine, from work previously reported and from some work of his own, that addition is not effected with the linking group CHX (X being the halogen), nor with a tertiary group CX, nor if a secondary or tertiary substituted group be present in the compound. Addition is not obtained with ethylidene bromide, nor with common propylene bromide,  $\text{CH}_3\text{CHBr.CH}_2\text{Br}$ , nor with monobromomethylene, nor with either *alpha* or *beta* monobromopropylene, nor with  $\text{CHBr:C(CH}_3)_2$ . In failure of addition other reactions take place, the products of which have been determined. Evidently the affinities of these

<sup>1</sup> N. Menshutkin and M. Vasileff, St. Petersburg, April, 1890: *Ztschr. phys. Chem.*, 5, 549.

<sup>2</sup> Menshutkin, 1895: *Ber. d. chem. Ges.*, 28, 1398.

<sup>3</sup> G. Bredig, 1894: *Ztschr. phys. Chem.*, 13, 288.

<sup>4</sup> G. Kleine, 1894: *Chem. Centrbl.*, I, 16, from *Ztschr. Naturwissenschaften*, 66, 1-72.

other products are factors in the problem as to the limits of alkyl union with nitrogen in organic bases.

In the studies of these limits phenyl has received less attention.<sup>1</sup> Diphenylamine is a weak base. Triphenylamine is indifferent to acids, and refuses addition with alkyl iodides. Triphenyl phosphine is stated to have a little capacity to hold alkyl iodides in union. Coming under the definition of a tertiary alkyl, phenyl has base-forming capacity distinctly greater than that of tertiary butyl, the interactions of all the CH groups in the ring in some way reinforcing the carbon which links to nitrogen, destitute as this carbon is in respect to direct hydrogen union. In pyridine there appears an altogether different character, an indivisible tertiary base of strength, with special additive capabilities. With alkyl iodides it forms certain addition compounds beyond those obtained even with trimethylamine. In pyridine the carbon linked to nitrogen is wholly in CH groups, and we may infer that all of the five of these groups are in some sense directly united to the nitrogen, though brought within a valence of three. Possibly also, the unsaturation of the unions of carbon to carbon, which is more active in pyridine than in benzene, imparts additive power to the nitrogen. The vigorous formation of pyridine methyl iodide was remarked by Anderson<sup>2</sup> shortly after his discovery of this base.

Mention of the addition compounds of pyridine with methyl iodide,<sup>3</sup> ethyl iodide,<sup>4</sup> propyl iodide and isopropyl iodide,<sup>5</sup> has been published in the accounts of various investigations devoted to other subjects, and therefore with partial examination and description of these particular products.<sup>6</sup> In resorting to pyridine as an analytical reagent for the identification of alkyls, Lip-

<sup>1</sup> In setting out to build up secondary and tertiary amines in 1850, A. W. Hofmann formed ethylphenylamine, remarking that his "previous experimental researches suggested aniline for the foundation."—*Phil. Trans.*, 1850, I., 97.

<sup>2</sup> *Trans. Roy. Soc. Edinb.*, 21, (4) 571; *Ann. Chem. (Liebig)*, 94, 360.

<sup>3</sup> O. Lange, On picolines by Ladenburg's transposition, 1885: *Ber. d. chem. Ges.*, 18, 3436.

<sup>4</sup> O. de Coninck, Analytical distinction between pyridine and quinoline, 1883: *Bull. Soc. chim.* [2], 40, 276.

<sup>5</sup> Ladenburg and Schraeder, On formation of propyl pyridines, 1884: *Ber. d. chem. Ges.*, 17, 1121, and further in other papers.

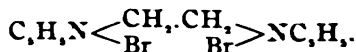
<sup>6</sup> A description of these four quaternary base iodides is given in another paper from this laboratory by A. B. Prescott.

ger<sup>1</sup> has recently reviewed the literature upon pyridine alkyl iodides and has also contributed an account of the preparation, and certain of the properties of the obtainable butyl iodides of pyridine, namely, those of normal butyl, isobutyl, and secondary butyl. Tertiary butyl iodide did not form a permanent addition product with pyridine. In Lippert's hands, the reaction for its production yielding indications of pyridine hydriodide and of isobutylene. These transformation products are the same that have been obtained upon attempting to introduce tertiary butyl into aliphatic amines, and at all events have prevented the linking of more than one tertiary butyl group to the nitrogen of these amines.

It appears, therefore, that for secondary and tertiary alkyl halides, the limits of pyridine addition go beyond the limits of trimethylamine or triethylamine addition, while the former limits are parallel to the latter. On the other hand it is easier to form a primary amine or ammonium salt of a tertiary alkyl than it is to form a pyridinium salt of the same alkyl. Comparing pyridine addition with aliphatic base formation, we may apply the conclusions drawn by Menschutkin from comparisons among certain aliphatic bases themselves, that the capacity of the nitrogen atom in a base to exercise five units of valence, depends largely, he says, on the nature of the elements or groups to which the nitrogen is already united.

#### DIHALOGEN SUBSTITUTED HYDROCARBONS IN ADDITIVE REACTION WITH PYRIDINE.

The action of halides of "diatomic radicals" upon the tertiary amines was studied by Hofmann in London.<sup>2</sup> Pyridine ethylene bromide was obtained<sup>3</sup> in his laboratory a short time before he returned to Germany. This product was stable, and upon analysis was found to have the proportions of  $(C_5H_5N)_2$ ,  $C_2H_2Br_2$ . We may now express this composition by the formula



<sup>1</sup>W. Lippert. On the decomposition of ethers by hydrogen halides, 1893: *Ann. Chem. Liebigs*, 276, 151.

<sup>2</sup>Phil. Trans. Action of ethylene bromide upon trimethylamine, May 2, 1858, upon triethyl phosphine June 25, 1860. Further Proc. Roy. Soc., 9, 203.

<sup>3</sup>Davidson May 24, 1861, Proc. Roy. Soc., 11, 261; *J. Chem. Soc.*, 14, 161.

The next homologue in diprimary dibromine substitution is trimethylene bromide,  $\text{CH}_2\text{Br}.\text{CH}_2.\text{CH}_2\text{Br}$ , and we have obtained its addition compound with pyridine as follows: Pyridine of a boiling-point of  $116^\circ\text{--}118^\circ\text{C}$ ., and trimethylene bromide of a boiling-point of  $165^\circ\text{C}$ ., were added together in the proportion of two molecules of the pyridine to one molecule of the bromide, and to the mixture one-fifth its volume of absolute alcohol was added. In Preparation I the mixture was heated in a sealed tube, at  $105^\circ\text{--}115^\circ\text{C}$ . for four hours, when the product was a light brown crystalline mass, with a very little dark brown oily liquid and some gas escaping as the tube was opened. The crystals were drained, washed with alcohol, becoming of very light color, and recrystallized once from alcohol, becoming nearly white. Dried on a porous plate, the melting point of the crystals was  $225^\circ\text{--}226^\circ\text{C}$ . In Preparation II the same materials, in same proportion, were digested in a sealed tube without applying heat, for a week. Crystallization began in clusters on the first day and increased steadily until apparently complete, this product being pure white. These crystals, without recrystallizing, were washed under suction with alcohol and dried on a porous plate in a vacuum desiccator. The melting point was the same as that of Preparation I.

This compound is very soluble in water, less soluble in alcohol, and in ether, and but very slightly soluble in chloroform. It is slightly hygroscopic in the air. Kept in an open vessel for weeks it shows no indication of decomposition. At the high melting point there is gradual decomposition. Distilled at a little above its melting point, it yielded hydrobromic acid, and a very hygroscopic sublimate, which sublimed again unchanged, and had the properties of pyridine hydrobromide. No further work was done upon the decomposition products. Analysis of the addition product itself gave figures as follows:

	Calculated for ( $\text{C}_5\text{H}_5\text{N}$ ) $_2\text{C}_3\text{H}_6\text{Br}_2$ .	Preparation I.		Preparation II.
		(1)	(2)	
Bromine .....	44.43	44.11	44.07	44.42
Nitrogen .....	7.78	8.08	8.46	7.84

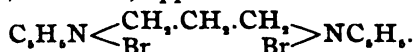
A determination of the molecular weight was made with Preparation I by the cryoscopic method, using phenol as the solvent. Previous trial was made with acetic acid, the results of

which indicated decomposition of the addition product. Had time permitted making the determination with the purer product in Preparation II, obtained later, results closer to the calculated molecular weight than could have been expected. The figures obtained with Preparation I were as follows, in which  $M$  = molecular weight;  $K$  = constant, which for phenol is 76;  $g$  = grams of substance;  $G$  = grams of solvent, and  $\Delta$  = depression.

These are taken in the formula  $M = 100.K. \frac{g}{\Delta G}$ .

No.	$g$ .	$G$ .	$\Delta$	$M$ .
1.....	0.4055	15.5	0.573°	346.8
2.....	0.6898	15.5	1.083°	312.0
3.....	0.2339	16.6	0.328°	328.0
4.....	0.3386	15.7	0.492°	332.8
5.....	0.3852	24.8	0.340°	347.1
6.....	0.6914	24.8	0.651°	326.0
$(C_5H_5N)_2C_3H_6Br_2$ .....				359.15

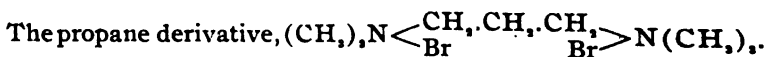
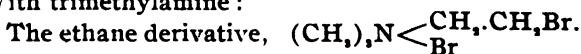
The formula, therefore, appears to be



This determination supports the formula adopted for the pyridine ethylenebromide of Davidson, as a dipyridine compound. Hofmann<sup>1</sup> found the trimethylamine ethylenebromide to have the proportions of a monammonium compound,  $(CH_3)_3N.C_2H_5Br_2$ , while, singularly enough, Kleine gives<sup>2</sup> the proportions in trimethylamine trimethylenebromide to be those of a diammonium compound  $((CH_3)_3N)_2.C_3H_6Br_2$ .

The composition of these four related dihalogen addition products, the aliphatic base and the aromatic base combinations respectively with substituted ethane and propane, may be compared as follows:

With trimethylamine:



With pyridine:



<sup>1</sup> 1858: Proc. Roy. Soc., 9, 293. "Addition of nitrate of silver precipitates only one-half of the bromine as bromide of silver, while even by protracted ebullition the second half remained untouched."

<sup>2</sup> Chem. Centrbl., 1894, I., 16.

The propane derivative,  $C_3H_5N \begin{smallmatrix} CH_3 \cdot CH_2 \cdot CH_2 \\ Br \quad \quad Br \end{smallmatrix} > NC_3H_5$ .

As these results now stand, it appears, *first*, that pyridine is more reactive for addition with diprimary halogen groups than is trimethylamine; *second*, that with the weaker base the one primary halogen group protects the other from addition when both these groups link together, not when they are separated by a  $CH_2$  group. In this relation it may be noted as a conclusion of Bredig,<sup>1</sup> that in metameric diamines, the bases are stronger, the further removed are the amido groups.

We have studied the reaction of pyridine upon a few primary-secondary dihalogen substituted hydrocarbons, and have not obtained addition in any of these cases. The conditions of addition were digestion in sealed tubes at  $80^\circ$  to  $100^\circ$  C. Propylene bromide,  $CH_3 \cdot CHBr \cdot CH_2Br$ , was treated in several operations, both with di-pyridine proportions and with mono-pyridine proportions, with the result of various products, but without an addition product. Pyridine hydrobromide was at all events obtained. Again, with ethylidene chloride no addition was obtained. Other conditions, however, will be brought to bear upon this class of pyridine additions, in work now in hand in this laboratory.

ANN ARBOR, MICHIGAN.

## A PROPOSED SCHEDULE OF ALLOWABLE DIFFERENCE AND OF PROBABLE LIMITS OF ACCURACY IN QUANTITATIVE ANALYSES OF METAL- LURGICAL MATERIALS.<sup>2</sup>

BY E. D. CAMPBELL.

Received October 1, 1895.

**W**ITHIN the past twenty years, metallurgical practice has grown to depend more and more upon a chemical knowledge of the material employed in the various operations. On account of this dependence it has become necessary to have accurate as well as rapid methods for the determination of the elements which take an active part in the different processes.

Many methods for the determination of the various elements

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Read before the Chemical Section of the American Association for the Advancement of Science. Sept. 2, 1895.

usually met with in metallurgical work have been proposed, each having its own claim for accuracy, or rapidity, or both, but as will be seen from the efforts of the International Committee on the analysis of Iron and Steel, we are far from having perfect methods for metallurgical analysis.

There are many sources of error in ordinary quantitative determinations, which, while they can be partially avoided, can never be wholly overcome. Among these may be mentioned such errors as arise from solubility of precipitates, solubility of apparatus in which operations are performed, impurities in chemicals, inaccurate graduation of volumetric apparatus, unavoidable error in accuracy of weighing, and last, but not least, errors due to what may be termed the personal equation, the presence or absence in the operator of that manipulative skill which distinguishes an expert from a clumsy worker. Since we cannot expect absolute agreement in results it may be asked how close should quantitative determinations agree. This question cannot be answered by a single figure since the unavoidable errors in the various determinations differ according to the element determined and the method used in the analysis. Just how great a difference between determinations should be allowed and what the probable limit of accuracy, which may be hoped for, is largely a matter of judgment based upon the examination of the results obtained by different chemists, known to be careful operators, working upon the same material.

Basing our judgment upon the usual errors of analysis, upon the commercial requirements of accuracy and upon the unavoidable sources of error we would propose the following schedule of allowable differences and of probable limits of accuracy for discussion in the section. In the table below the first column shows the element or constituent determined; the second, a formula for calculating the difference which might be reasonably expected between the results of two chemists working upon the same material and the third column shows a formula for calculating the probable minimum error which may be hoped for. To take an instance: suppose chemist A reports the phosphorus in a specimen of steel as 0.076 per cent, then by the formula in the table we might expect B to report  $0.076 \pm 0.00352$  per cent.,



and from the third column we could not hope to reduce the error to less than 0.00058 per cent.

Element or constituent.	Allowable difference of per cent.	Probable limit of accuracy.
<i>Iron and Steel.</i>		
Graphitic carbon	$\pm[0.050+(0.02 \times \text{Cg})]$	$\pm[0.005+(0.005 \times \text{Cg})]$
{ Cast iron	$\pm[0.050+(0.02 \times \text{Cc})]$	$\pm[0.005+(0.005 \times \text{Cc})]$
{ Combined carbon		
Carbon in steel	$\pm[0.010+(0.02 \times \text{C})]$	$\pm[0.002+(0.003 \times \text{C})]$
Silicon	$\pm[0.005+(0.02 \times \text{Si})]$	$\pm[0.002+(0.003 \times \text{Si})]$
Sulphur	$\pm[0.003+(0.03 \times \text{S})]$	$\pm[0.0005-(0.005 \times \text{S})]$
Phosphorus	$\pm[0.002+(0.02 \times \text{P})]$	$\pm[0.0002+(0.005 \times \text{P})]$
{ Manganese in	$\pm[0.005+(0.04 \times \text{Mn})]$	$\pm[0.001+(0.005 \times \text{Mn})]$
{ cast iron and steel		
{ Manganese in	$\pm[0.050+(0.004 \times \text{Mn})]$	$\pm[0.005+(0.001 \times \text{Mn})]$
{ spiegels, ferro, etc.		
Nickel	$\pm[0.050+(0.02 \times \text{Ni})]$	$\pm[0.005+(0.005 \times \text{Ni})]$
<i>Ores.</i>		
Silica	$\pm[0.050+(0.006 \times \text{SiO}_2)]$	$\pm[0.005+(0.001 \times \text{SiO}_2)]$
Alumina	$\pm[0.030+(0.003 \times \text{Al}_2\text{O}_3)]$	$\pm[0.005+(0.001 \times \text{Al}_2\text{O}_3)]$
Ferric oxide	$\pm[0.030+(0.003 \times \text{Fe}_2\text{O}_3)]$	$\pm[0.005+(0.001 \times \text{Fe}_2\text{O}_3)]$
Iron	$\pm[0.020+(0.003 \times \text{Fe})]$	$\pm[0.004+(0.001 \times \text{Fe})]$
Manganese	$\pm[0.050+(0.003 \times \text{Mn})]$	$\pm[0.005+(0.001 \times \text{Mn})]$
Calcium oxide	$\pm[0.050+(0.002 \times \text{CaO})]$	$\pm[0.010+(0.001 \times \text{CaO})]$
Magnesia	$\pm[0.050+(0.010 \times \text{MgO})]$	$\pm[0.005+(0.002 \times \text{MgO})]$
Phosphorus	$\pm[0.002+(0.02 \times \text{P})]$	$\pm[0.0002+(0.005 \times \text{P})]$
Phos. pentoxide	$\pm[0.005+(0.02 \times \text{P}_2\text{O}_5)]$	$\pm[0.0005+(0.005 \times \text{P}_2\text{O}_5)]$
Combined water	$\pm[0.050+(0.10 \times \text{H}_2\text{O})]$	$\pm[0.010+(0.001 \times \text{H}_2\text{O})]$
{ Potassium oxide	$\pm[0.050+(0.020 \times \text{K}_2\text{O})]$	$\pm[0.005+(0.005 \times \text{K}_2\text{O})]$
{ Sodium oxide		
Sulphur in iron ore	$\pm[0.005+(0.030 \times \text{S})]$	$\pm[0.001+(0.003 \times \text{S})]$
Sulphur in pyrite	$\pm[0.050+(0.004 \times \text{S})]$	$\pm[0.005+(0.0002 \times \text{S})]$
Lead	$\pm[0.050+(0.003 \times \text{Pb})]$	$\pm[0.005+(0.0005 \times \text{Pb})]$
Zinc	$\pm[0.050+(0.003 \times \text{Zn})]$	$\pm[0.005+(0.0005 \times \text{Zn})]$
Copper	$\pm[0.030+(0.003 \times \text{Cu})]$	$\pm[0.005+(0.001 \times \text{Cu})]$
Nickel	$\pm[0.030+(0.003 \times \text{Ni})]$	$\pm[0.005+(0.001 \times \text{Ni})]$
{ Arsenic	$\pm[0.050+(0.010 \times \text{As})]$	$\pm[0.002+(0.001 \times \text{As})]$
{ Antimony		
Tin	$\pm[0.010+(0.010 \times \text{Sn})]$	$\pm[0.005+(0.001 \times \text{Sn})]$
<i>Coal and Coke.</i>		
Moisture	$\pm[0.050+(0.020 \times \text{H}_2\text{O})]$	$\pm[0.005+(0.005 \times \text{H}_2\text{O})]$
Vol. hydrocarbon	$\pm[0.050+(0.010 \times \text{hydro})]$	$\pm[0.010+(0.001 \times \text{hydro})]$
Fixed carbon	$\pm[0.050+(0.010 \times \text{C})]$	$\pm[0.010+(0.001 \times \text{C})]$
Sulphur	$\pm[0.020+(0.030 \times \text{S})]$	$\pm[0.005+(0.003 \times \text{S})]$
Ash	$\pm[0.050+(0.005 \times \text{Ash})]$	$\pm[0.005+(0.001 \times \text{Ash})]$
Phosphorus	$\pm[0.002+(0.02 \times \text{P})]$	$\pm[0.0002+(0.005 \times \text{P})]$

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 10.]

## DERIVATIVES OF COLUMBIUM AND TANTALUM.<sup>1</sup>

BY MARY ENGLE PENNINGTON.

Received November 29, 1895.

Among the more metallic members of Group V of the Periodic System are the elements columbium and tantalum, which, though almost a century old and counting among their devotees such investigators as Rose, Hermann, Marignac, Rammelsberg, and others of equal fame, still offer many interesting problems to the student of inorganic chemistry. Comparatively few of the compounds of these elements have been prepared. Those which have been studied narrowly enough to afford an accurate knowledge of their chemical behavior form a much shorter list. The early literature is, in many instances, very contradictory, due to the supposed existence of such elements as pelopium and ilmenium, engendering as they did the fruitful controversy between Hermann and Marignac, which controversy resulted in the tacit acceptance by the chemical world of Marignac's statement, that columbium is elementary. The old doubt, however, appears to have been revived through the very careful work of Krüss in 1887, on the oxides of these metals, their separation from each other and also from the oxides which accompany them in their apparent minerals.

He found through the fractional crystallization of the double fluoride of columbium and potassium, and by determining the atomic value of the various fractions, that something apparently contaminated the columbium. In some fractions the values obtained were far too low. This he accounted for by proving the presence of titanium. Other portions, however, were much too high, and this, it was carefully proved, was not due to adhering tantalum. Just what the substance was which gave in one fraction an  $R'$  having almost double the accepted atomic mass was left undecided.

A careful consideration of this question in the light of the various researches, makes it seem not improbable that the compounds of columbium, as we know them, are not perfectly free

<sup>1</sup> From the author's thesis presented to the University of Pennsylvania for the degree of Ph.D., 1895.

from contaminating substances. The many difficulties encountered in the separation of this oxide from others usually occurring with it, and the insufficiency of the prevailing methods of separation, seem to demand a more exact knowledge of the behavior of the element in the purest condition obtainable, and also when mixed with the oxides of tantalum and titanium which usually adhere to it.

It was with the hope that some additional light might be thrown upon the general deportment of the derivatives of these elements that this research was undertaken.

The material used was obtained from a columbite from Wakefield, N. H. An abundant supply of the mineral was secured through the kindness of Professor S. P. Sharples, of Boston, in whose possession it had been for some years though it had never been analyzed. Wakefield is a new locality for columbite. The deposit was discovered while mining for feldspar. Near the columbite is quite a deposit of beryl.

#### ANALYSIS OF WAKEFIELD COLUMBITE.

The mineral occurs in large, black, lusterless masses. Scattered over the surface are little patches of a bright yellow substance. These proved to be uran-ochre and gave evidence of the presence of the uranium which was later found in the mineral. Feldspar occasionally penetrated the mass, though in small quantity. The specific gravity of picked material was found to be 5.662 at 4° C.

Decomposition was effected by the method usually employed for this class of minerals.

*Fusion with Acid Potassium Sulphate.*—The finely divided mineral was allowed to stand over calcium chloride for some hours. The desired amount of this dry, and almost impalpable, powder was weighed off and mixed with at least nine times its weight of fused potassium bisulphate. This must be an intimate mixture. Great care should be exercised when the heat is first applied, else loss by spattering will occur. Frequent stirring tends to prevent this, and also hastens the decomposition.

Some trouble was experienced by the fusion "climbing" and

leaving far up on the sides of the crucible particles of mineral which could neither be driven down by heat or forced down by a platinum rod. To collect these particles the crucible containing the clear, quiet fusion was slightly tilted and the adhering portions covered with a little bisulphate. Then by gently heating the whole mass was driven down until it met the main portion of the fusion. All decompositions by this method were made in a large platinum crucible or platinum dish. The latter was preferred. If the mineral is fine enough the fusion is complete in about five hours.

The fused mass was taken up in a large quantity of water, and boiled out with water several times. The insoluble portion consisted of the oxides of columbium, tantalum, titanium, tin, tungsten, and any silica which was present. Small quantities of these oxides invariably remained dissolved although the solution was boiled for a long time; it is, therefore, advisable to let the filtrate stand twenty-four hours, then refilter.

The moist oxides, according to Headden,<sup>1</sup> should "be digested with yellow ammonium sulphide" to remove all tin, tungsten, etc. Rose recommends that yellow ammonium sulphide should be simply poured over them, and that this solution should be evaporated to dryness, and gently ignited, to render the columbium and tantalum oxides which have been dissolved by the alkali, insoluble. Wöhler<sup>2</sup> claims that it is sufficient to treat the metallic oxides upon the filter with yellow ammonium sulphide. As some uncertainty existed as to the best course to pursue, the effect of ammonium sulphide when mixed with these oxides for a longer or shorter period of time was studied.

Heating in a porcelain dish on the water-bath for three hours gave 1.15 per cent. of the mixed oxides; one and one-half days, 1.60 per cent.; three days, 1.85 per cent.; one week, 2.24 per cent. By pouring the sulphide over the oxides on the filter, as Rose and Wöhler advise, 0.24 per cent. of the mixed oxides was obtained.

Apparently, the moist metallic oxides are more readily dissolved by ammonium sulphide than is generally supposed, and,

<sup>1</sup> *Am. J. Sci.*, 41, 91, 1891.

<sup>2</sup> *Mineral Analyze*, p. 140.

therefore, when working with columbites containing the acid oxides care must be taken, or a very appreciable error may result.

The ammonium sulphide solution was precipitated by dilute hydrochloric acid, and the precipitate was filtered, and washed with hydrogen sulphide water, alcohol, ether, carbon disulphide and ether. The mixed sulphides were carefully heated in the air, then reduced in a current of hydrogen gas. The residue treated with dilute hydrochloric acid gave tin in solution and left undissolved a small quantity of a black compound which proved to be the tetroxide,  $\text{Cb}_2\text{O}_4$ , with possibly a little tantalum.

The moist oxides when treated with ammonium sulphide have not only the acids removed, but the iron contained in them is changed to sulphide. This is dissolved out by dilute sulphuric acid. Filter off the oxides and wash them thoroughly with boiling water. A pump is usually necessary because of the precipitate being finely divided, and having a tendency to clog the pores of the filter. By this treatment the oxides should be entirely freed from iron and manganese. Nevertheless ignition gave a powder having a distinct pinkish yellow hue, showing the presence of these elements. The oxides were, therefore, re-fused with potassium bisulphate and treated as before. The second fusion gave a product lighter in color, yet not perfectly white. Another fusion was resorted to, and no loss in weight was observed, as a small amount of iron still adhered to the oxides. In fact, a *perfectly white* mixture of the oxides has not been obtained by this method.

The sulphuric acid solution of the iron which remained with the insoluble oxides, was added to the aqueous extraction of the fusion. This solution now contained iron, manganese, uranium, and calcium, with a large excess of sulphuric acid and alkali salt. Yttrium, cerium, and calcium were looked for according to the plan presented in Rose's Handbuch der analytischen Chemie, 2, 335, which is, in brief, this: The greater part of the free acid is neutralized with sodium carbonate; sodium acetate is added, so that acetic acid is in large excess. The earths are precipitated by ammonium oxalate, the precipi-

tate being allowed to stand twenty-four hours. From three grams of mineral only a very small amount was obtained. This was too small a quantity to investigate further, so that if any rare earths are present in the mineral they exist in traces.

To the filtrate which contained iron, manganese and uranium were added ammonium sulphide and ammonium carbonate. The iron and manganese were precipitated as sulphides, while uranium was held back by the ammonium carbonate. Beryllium, if present, would have been found here. This element was sought for, since the locality from which the mineral came made it a probable constituent, but none was detected. The sulphides having been filtered out, the filtrate was made acid with hydrochloric acid, the carbon dioxide boiled off, then the uranium precipitated by ammonium hydroxide. The uranium hydrate was filtered, washed, ignited, and weighed as  $U_2O_5$ . The sulphides of iron and manganese were dissolved off the filter in hydrochloric acid, oxidized, and separated by the basic acetate method, the manganese being finally weighed as manganese pyrophosphate.

The water contained in this columbite was determined by heating in a boat in a glass tube, and collecting the aqueous vapor in a weighed calcium chloride U tube.

In the literature relating to columbites and allied minerals, while a ferrous content is given, the method by which it was determined is omitted. Perhaps this is due to the fact that the customary decomposition with sulphuric acid in a sealed tube naturally suggests itself, yet in applying this course to the columbite under examination unexpected difficulties were encountered. The experience is at least interesting.

The mineral was ground very fine and heated in sealed tubes with sulphuric acid (one part of concentrated acid to two parts water), the resulting decomposition being titrated with permanganate with the following results :

	Per cent. $FeO$ .
0.5 gram heated one day at $210^{\circ} C$ .....	1.316
0.5 gram heated two days at $230^{\circ} C$ .....	1.416
0.5 gram heated five days at $230^{\circ} C$ .....	5.50

It seemed probable that this was not the total amount of fer-

rous iron in the columbite, hence attention was directed to an old method which is rarely used, yet seems to be worthy of greater attention than has been given it. Berzelius first suggested the method, though it is generally credited to Hermann. The finely ground mineral is mixed with fused and finely divided borax. A small platinum crucible is completely filled with this mixture, then covered with a platinum lid, and the whole placed in a larger platinum crucible. Dry magnesium oxide is packed around and over the inner crucible until it is completely covered and so excluded from air contact. The heat of a good Bunsen lamp is applied for one-half hour, when the decomposition is complete. Longer heating, or too rapid cooling, causes the fusion to adhere very tightly to the crucible, and loss may result on endeavoring to remove it. When the whole is quite cold, the small crucible is taken out, freed from adhering magnesium oxide, and weighed. The fusion, which is a clear green glass, is then freed from the crucible by sharply tapping; a piece may be broken off, weighed, ground in a mortar, dissolved in water and sulphuric acid, and titrated with potassium permanganate. Or, if the amount of ferrous iron is not large, it is better to crush the whole fusion in a diamond mortar, then place in a flask provided with a Bunsen valve, dissolve in water and sulphuric acid, and titrate. To prevent the oxidation of the iron during its solution, a quantity of sodium carbonate was placed in the flask with the ground fusion, and the water and sulphuric acid added carefully to this mixture. When a strong evolution of carbon dioxide had continued for several minutes, the cork carrying the Bunsen valve was quickly inserted, and the flask put aside until solution had taken place. It is necessary to shake the flask from time to time, otherwise the finely divided oxides which separate will enclose some particles of the fusion, and the result will be low. In one or two hours the insoluble residue should be a perfectly white, fine, homogeneous mass. The flask is then opened, more sulphuric acid added if necessary, and the iron titrated with permanganate. A number of fusions were made according to this method, the amount of ferrous oxide found being 6.426 per cent. The method seems to be, so far as columbite is concerned, perfectly trustworthy. It

is rapid, and the manipulation is not difficult. The oxides which separated out were perfectly white. In one experiment they were filtered off, washed with hot water, ignited, and weighed. The percentage of mixed oxides, 77.94 per cent., agrees quite well with that obtained by the bisulphate method.

The quantitative analysis of this columbite by fusing with bisulphate, as above described, gave the following results :

	A.	B.	C.	D.	E.
$\left. \begin{array}{l} \text{Ta}_2\text{O}_5 \\ \text{Cb}_2\text{O}_5 \\ \text{TiO}_2 \end{array} \right\}$ .....	78.61	79.04	79.00	77.96	78.70
$\text{Fe}_2\text{O}_3$ .....	12.30	13.83	13.62	13.58	....
$\left. \begin{array}{l} \text{SnO}_2 \\ \text{WO}_3 \end{array} \right\}$ .....	1.15	1.60	1.85	2.24	1.84
$\text{MnO}$ .....	8.96	8.32	....	8.08	....
	<u>101.02</u>	<u>102.79</u>	<u>....</u>	<u>100.86</u>	<u>....</u>

One-half gram of material was used in each case. The ferric oxide, as given above, includes the ferrous, which, estimated by the method of Berzelius, equals 6.42 per cent.

In a sixth analysis three grams of material were taken, and due attention was paid to those constituents which former analyses had shown to be present, but in such small quantities that their determination was not trustworthy. The results in this case were :

	Per cent.
$\left. \begin{array}{l} \text{Ta}_2\text{O}_5 \\ \text{Cb}_2\text{O}_5 \\ \text{TiO}_2 \end{array} \right\}$ .....	78.04
$\left. \begin{array}{l} \text{WO}_3 \\ \text{SnO}_2 \end{array} \right\}$ .....	0.24
$\text{U}_3\text{O}_8$ .....	0.48
$\text{Fe}_2\text{O}_3$ .....	5.22
$\text{FeO}$ .....	6.42
$\text{CaO}$ .....	0.02
$\text{MnO}$ .....	8.96
$\text{H}_2\text{O}$ .....	1.22
Total .....	<u>100.60</u>

An interesting point in the composition of this columbite is the ferric oxide. Hermann records one analysis of some fragments of a columbite from Miask containing several per cent. of it, and so far as I am aware this is the only columbite in which



this constituent is mentioned. He also gives a Miask columbite containing 0.50 per cent. of uranium oxide. Genth mentions a trace of uranium in a columbite analyzed by him.

While no effort was made to separate the metallic oxides quantitatively, it was found from the preparation of pure material that the columbium was in decided excess. Titanic acid was proved to be present, and silica was found in very small quantities.

Many of the recorded analyses in which separations of columbic and tantalic oxides are given, fail to state whether any attempt had been made to eliminate or to prove the presence of titanium or silica. Given a mixture of tantalum, columbium, and titanium, the analyst will have no difficulty in separating tantalum from columbium by Marignac's double fluoride method. But the titanium double fluoride, when mixed with the columbium salt, shows an abnormal solubility which makes its separation very doubtful. This point will be more fully discussed later.

*Fusion with Sodium Thiosulphate.*—It occurred to me to try the decomposition of the mineral by fusion with sodium thiosulphate, believing that in this way tungsten and tin would be converted into sulpho salts, and could then be more effectually removed from the other constituents. Without entering into detail, I may say the attempt was fruitless.

*Decomposition by the Gibbs Method.*—Some years ago Dr. Gibbs published a procedure<sup>1</sup> for the decomposition of the columbite minerals; and as my desire was to investigate the different methods of decomposition, I naturally turned to this suggestion. In mineral literature this course is given a second place to the bisulphate decomposition. My own experience compels me to prefer it to the latter method. The details of the Gibbs method are, in brief, as follows:

The mineral must be fine, yet need not be in an impalpable powder, as is necessary in the bisulphate decomposition. It was intimately mixed, by grinding in a mortar, with three times its weight of potassium fluoride; the mixture was transferred to a platinum crucible and made into a paste with concentrated

<sup>1</sup> *Am. J. Sci. Arts.*, 37, 357. 1864.

hydrofluoric acid. The mass heated up at once, and for some minutes the decomposition proceeded without the application of heat. It was found advantageous to let this mixture of acid salt and mineral stand for several hours, stirring occasionally, and adding more acid if the mass became hard. It was then heated on a water-bath until the excess of acid was driven off. After thoroughly drying on an iron plate, the free flame was applied. Hydrofluoric acid was driven out of the acid potassium fluoride, and at length the whole mass fused and formed a clear, quiet, easily handled fusion, which, upon cooling, became a beautiful pink-violet in color.

The decomposition is not complete until every part of the mixture has assumed this color, which does not change on further heating. In the early part of the fusion a deep blue color appears. If the action be interrupted at this point, an incomplete decomposition will result.

The violet mass was taken up with water and hydrofluoric acid in a platinum dish, then boiled and filtered. This extraction should be repeated several times. If the decomposition is not quantitative, the solution in water is much hastened by first grinding the fusion. Any silica which may have been present in the mineral will remain as potassium silicofluoride. This being a gelatinous compound, it is likely to enclose fine particles of the fusion and prevent their solution. If the amount of silica is not large, a separation may usually be effected by treating with concentrated hydrofluoric acid; but if much silica be present it is safer to evaporate to dryness with a little sulphuric acid, and take up the remaining potassium sulphate with water. If any insoluble substance is left it may be dissolved in hydrofluoric acid and added to the main portion of the solution.

If an analysis of the mineral is desired, hydrogen sulphide gas may now be passed through the acid filtrate, whereby any tin, tungsten, or molybdenum present will be precipitated as sulphide. Filter, and separate as usual.

The filtrate was evaporated to dryness, and enough sulphuric acid added to expel all the hydrofluoric acid. The excess of acid was driven off on an iron plate, not over a free flame, and the oxides of columbium, tantalum, and titanium precipitated

by boiling with a large quantity of water. The boiling must be continued for several hours to insure a complete precipitation, but it is not so difficult to bring down the metallic oxides under these conditions as in the bisulphate decomposition. Filter, and wash the oxides with hot water, first by decantation, then on the filter. The ignition of the oxides gave a *perfectly white*, fine powder; and this fused with sodium carbonate or potassium fluoride yielded a colorless mass when cold. The oxides obtained from the bisulphate never did so, but formed with the carbonate a tinge of green, and with the fluoride a tinge of pink, showing the presence of manganese and probably of iron.

The filtrate from the mixed oxides contained iron, manganese, and uranium. These were separated by ammonium sulphide and ammonium carbonate, following the plan given under the bisulphate method.

When the object is simply the extraction of pure mixed oxides, the above procedure may be somewhat varied. The fusion is made just as usual, then taken up with water insufficient for perfect solution, and a small quantity of hydrofluoric acid, boiled, and filtered. On cooling, the filtrate will be found to be an almost solid mass of the columbium double fluoride,  $2\text{KF} \cdot \text{CbOF}_2 \cdot \text{H}_2\text{O}$ , which separates as a beautiful shining salt and consists of thin laminae. At first the tantalum double fluoride remains undissolved, or is dissolved only in small quantity, as it is a very insoluble salt compared with the columbium compound, but if too much hydrofluoric acid is added the tantalum will be discovered with the columbium potassium fluoride, and larger amounts of iron and manganese will also contaminate it. From a very concentrated solution of the columbium double fluoride, such as would be obtained by this method, any tantalum double fluoride will, if present, separate almost immediately. These needles should be examined under a microscope for the thin transparent plates of the columbium salt. When these begin to appear, filter at once and use a pump. The plates are a good indication that all tantalum is separated. The filtrate, on standing, will usually give the columbium salt, but it may have to be concentrated a little. The first crop of crystals may be colored pink by manganese or iron. Recrystallization, how-

ever, removes this. The next crop is fairly pure. When working with large quantities, a very satisfactory approximate separation of columbium from tantalum may be obtained by this method of extraction.

As boiling with pure water, or even with water containing a small amount of hydrofluoric acid decomposes the tantalum potassium fluoride and leaves an insoluble compound,



while the columbium double salt is practically unaffected, this treatment leaves us in the end a white, finely divided mass, which is almost free from columbium. By heating this residue on a water-bath with a rather concentrated solution of hydrofluoric acid and a little potassium fluoride, the tantalum potassium fluoride is obtained and may be purified by recrystallization.

The Gibbs method was used for the preparation of rather large quantities of tantalum and columbium potassium fluorides. I think it preferable to the bisulphate decomposition and subsequent solution of the oxides in hydrofluoric acid, in that it does not consume so much time, and iron and manganese are more readily eliminated. The only objection is that large platinum vessels are needed; as a substitute for these, rubber beakers and funnels were sometimes used.

The method finally adopted is as follows:

*Separation of Columbium and Tantalum by their Potassium Double Fluorides.*—The pure mixed oxides were placed in a platinum crucible with three times their weight of potassium fluoride, then moistened with hydrofluoric acid as described under the decomposition of the mineral by the Gibbs method. By treating the fusion with water and hydrofluoric acid an almost perfect solution was obtained since only a trace of silica was present. Concentration gave the long pointed needles of tantalum potassium fluoride,  $2KF.TaF_5$ . These were filtered and the solution again concentrated. The crystal crop should be examined under the microscope as it may be a mixture of tantalum and columbium. Usually it is only tantalum.

If a considerable excess of hydrofluoric acid and potassium

fluoride is present in the mother-liquor, the next crop of crystals may be a complex mass about which the analyst can come to no definite conclusion. The fraction consists principally of long crystals much like the titanium double fluoride, and to make the matter more puzzling these crystals are not so soluble as those separating at the same time. They may be obtained pure by treating the mixture with a few drops of water and quickly filtering. Recrystallization from pure water gives the laminated salt  $2KF.CbOF_5.H_2O$ . If the acid and potassium fluoride are not in large excess, usually two, and sometimes three, crops of the laminated salt are formed, but in time the long needles are almost sure to make their appearance. These needles were tested for titanium, but no satisfactory evidence of its presence was obtained.

When the solution is very concentrated large, thin plates separate from it. These do not give the reaction with gallotannic acid, but they react with zinc, hydrochloric acid, and potassium thiocyanate. This test for columbium compounds will be noticed later. Recrystallization does not give the laminated salt. The crystals are always found, and are by no means in small quantity. With zinc and hydrochloric acid they give a greenish color which quickly becomes brown. They were repeatedly recrystallized, then decomposed with sulphuric acid. The oxide obtained was white and at  $19^{\circ}C$ . had a specific gravity of 4.57.

The oxide was placed in a platinum retort connected with a platinum condenser; hydrofluoric acid was poured over it and a free flame was applied. The volatile products were collected in water in a platinum dish. Several evaporations were necessary for the volatilization of this oxide. The solution in the dish was then treated with a small quantity of potassium fluoride and concentrated. The same large, thin plates crystallized out. These crystals were very beautiful, being frequently over an inch in length and one-half inch in width. They were so transparent that often their presence in the dish was altogether unnoticed.

Substance taken.	ANALYSIS.	
	$K_2SO_4$ found.	$Cl_2O_3$ found.
gram.	gram.	gram.
0.5000	0.5268	0.0059

This analysis would indicate that the salt is probably acid potassium fluoride with a small quantity of the double fluoride of columbium, yet it must not be forgotten that the reactions given above cannot be regarded as conclusive evidence of the presence of columbium.

Because of the brown color with zinc and hydrochloric acid these crystals were also tested for titanium. Its presence could not be detected.

#### QUALITATIVE REACTIONS.

Throughout this investigation the following questions constantly arose: How shall the purity of the columbium and tantalum compounds be determined? When is columbium free from tantalum? When is it free from titanium?

In the earlier work upon columbium we find Hermann describing a new element which he obtained from the mother liquors of the columbium potassium fluoride. This element, he states, gave a dark brown solution when reduced with zinc and hydrochloric acid, while the pure columbium compound gave a blue color. Both these solutions on standing in the air reverted to the white hydrate. Marignac replied that the brown color was not due to titanium but to titanium, a view which is now generally accepted.

He also declares that a brown color is produced when the potassium columbium oxyfluoride is treated with zinc and hydrochloric acid, the acid being in considerable excess. Then by treating with permanganate he found that an intermediate oxide had been formed to which he gave the formula  $Cl_2O_3$ .

Crystals of the columbium salt prepared as described above, continued to give this brown solution even after they had been subjected to five or six recrystallizations. Following the plan of Knudsen and Nielsen the atomic value of the oxide contained in such crystals was determined by decomposing with sulphuric acid, weighing the peroxide and the potassium sulphate, then

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by the ratio  $2 K_2SO_4 : Cb_2O_5$ , determining the value for  $Cb^V$ . This was found to be 85.7. Iron and manganese had been eliminated, titanium, therefore, was the probable cause of this low atomic value. The salt used was perfectly white, yielding a pure white oxide. This oxide was tested for titanium by the most delicate reactions known for the metal, but its presence could not be proved by any of them.

*1. Color and Reduction Reactions.* It has been found that the qualitative tests given in the various text-books for these three elements do not always hold good when the solution used is a double fluoride. As it is in this form that the separations are usually made, it has been thought advisable to note the action of some of the common reagents on these salts.

Gallotannic acid, which is considered the most characteristic test for columbium salts, behaves differently with different double fluorides. An acid solution of the laminated salt gives almost instantly, a deep, brick-red precipitate. The salt crystallizing in long needles gives a lighter red precipitate which does not separate so rapidly. The large, thin, transparent plates previously mentioned, give only a slight precipitate, and this is yellow in color. These reactions are most delicate if the salt be dissolved in water, a drop of hydrochloric acid added, then a little gallotannic acid dissolved in alcohol. After standing several hours all the precipitates assume the same color—a dark, brick red.

Tantalum double fluoride gives a sulphur yellow color with gallotannic acid. This, however, on standing becomes brick red, as the columbium does.

Titanium compounds are said to give a brownish color with gallotannic acid which changes quickly to an orange red. The potassium titanium fluoride gave a straw yellow color with this reagent; in time a flaky precipitate forms, but the color does not materially alter.

The following color reaction serves for the detection of very small quantities of columbium, and is applicable to any soluble columbium compound. An excess of potassium thiocyanate is added to a small quantity of the dissolved substance; then some pieces of zinc followed by strong hydrochloric acid. At

once the solution becomes a bright golden brown, which if much columbium be present may be almost red. A brisk and continued evolution of the gas does not alter this tint which is also stable for more than twenty-four hours in the acid solution. Neither titanium nor tantalum give any reaction with potassium thiocyanate under the above conditions.

Hyposulphurous acid,  $\text{H}_2\text{SO}_3$ , gives noteworthy color reactions with these salts. The tests were conducted in the following manner: A few cubic centimeters of a concentrated solution of sulphur dioxide were placed in a test tube provided with a cork, and granulated zinc was added. The liquid changed to a greenish color, and hydrogen was liberated. As soon as the evolution of the gas had ceased the solution containing the hyposulphurous acid was poured into the salt solution to be tested.

A solution of titanium double fluoride gave an orange yellow color at once. The oxide when treated in like manner became yellow.

Columbium double fluoride gave no color, but a white hydrate was soon precipitated. Columbic oxide gave a slight yellow tinge.

Tantalum double fluoride gave no color, but after standing a white precipitate separated. Tantalic oxide remained colorless when treated with hyposulphurous acid.

The white precipitates from the tantalum and columbium salts were probably hydrates due to the oxidation of the acid and its consequent action upon these salts.

Zinc and hydrochloric acid gave no reaction with the double fluoride of tantalum. With titanium a clear, delicate green was obtained. The columbium salts always gave a color with these reagents. The solution is at first dark blue, then a greenish brown, and finally a dark brown. Frequently a brown precipitate separates which on standing becomes white.

The hydrochloric acid solution of columbic oxide, and also the potassium columbium fluoride, were tested with hydrogen peroxide, this being accepted as one of the most delicate reagents for titanium. No yellow color in either case was obtained.



2. *Reactions with Wet Reagents.* A number of the ordinary reagents have been tried with these salts, the results being given in the following table. The reactions for the greater number are very different when the metal tested is as double fluoride. The ferrocyanides, in particular, have quite abandoned their ordinary colors with these compounds.

	2 KF. CbOF <sub>3</sub> . H <sub>2</sub> O.	2 KF. Ta F <sub>5</sub> .	2 KF. Ti F <sub>3</sub> .
Lead acetate.	White precipitate.	White precipitate.	White precipitate.
Mercuric chloride.	Slight precipitate in 24 hours.		
Mercurous nitrate	Yellow precipitate	Yellowish green precipitate.	Yellowish green precipitate. Precipitate soluble in water.
Potassium chromate.	White precipitate, soluble in H <sub>2</sub> O. Partly soluble in K <sub>2</sub> CrO <sub>4</sub> solution		
Potassium bichromate.		Precipitate after standing.	
Potassium cyanide	White precipitate on boiling.	White precipitate.	White precipitate.
Potassium ferrocyanide.	Green blue precipitate on boiling.	Yellow precipitate on boiling.	Precipitate on boiling.
Potassium thiocyanate.	White precipitate.	White precipitate, soluble in the cold. Comes down by boiling.	
Potassium iodide.	White, granular precipitate. Iodine is liberated.	White granular precipitate.	No precipitate, but iodine is liberated.
Disodium hydrogen phosphate.		White precipitate after standing.	White precipitate.
Silver nitrate.		White precipitate after standing.	
Sodium bisulphite	White precipitate.	White precipitate.	White precipitate.
Sodium pyrophosphate.		Slight cloudiness.	Precipitate.
Hypophosphorous acid.			
Sodium metaphosphate.			
Potassium bromide.	White precipitate.		

Disodium hydrogen phosphate, when added to titanium double fluoride, precipitates the titanium completely. The filtrate tested with ammonium hydroxide gave no precipitate. Columbium double fluoride, on the contrary, is not affected by this reagent.

After boiling a long time in a platinum dish a few white flocks were observed in the solution, but in such small quantity that they were disregarded. Whether this behavior may or may not be made the basis of a separation of these two elements is not yet determined, because of the difficulty in getting rid of the phosphoric acid. Fusion with sodium carbonate, extraction with water, and subsequent precipitation by sulphuric acid gives a mixture of sodium salt and columbic oxide. Some columbium remains in solution. Fusion with potassium acid sulphate is more satisfactory, yet is not complete.

DEPARTMENT OF TANTALUM, COLUMBIUM AND TITANIUM  
DOUBLE FLUORIDES TOWARD THE ELECTRIC CURRENT.

1. A solution of potassium columbium double fluoride,  $2 \text{KF} \cdot \text{CboF}_6 \cdot \text{H}_2\text{O}$ , in water, was treated with a small amount of sodium acetate. The precipitate formed was dissolved in acetic acid, and through this solution a current of one ampere, obtained from a thermopile, was conducted for five hours. A white precipitate, seemingly a hydrate, was formed. On breaking the current this rapidly went into solution.

2. (a) A solution of the salt in water was subjected to the same current for eight hours. Almost immediately the bottom of the platinum dish was covered with a blue deposit. This gradually spread over the whole surface exposed to the action of the current and became in a short time iridescent. As the deposit increased, the deep blue tint changed to more of a gray, and remained so until the current was broken. It was washed quickly with water then with alcohol and it was dried on the water bath.

0.0382 gram of the salt was taken, the deposit weighed 0.0282 gram. This white-looking substance did not alter in the air, but when heated to a red heat it was red shining, apparently oxide of columbium. It was readily soluble in hydrofluoric acid.

(b) A second experiment with 0.0382 gram of the substance, gave under the same conditions a deposit weighing 0.0388 gram. This white deposit of the salt formed to a white oxide weighing 0.0388 gram. The blue compound is in all probability, a lower fluoride of columbium.

3. The electrolysis of an aqueous solution of a sodium columbate gave a white, flocculent hydrate, not adherent to the dish. The precipitation was not complete. A current of one ampere was employed for a period of seven hours.

4. With a much stronger current (two amperes), a solution of the double salt  $2 \text{KF} \cdot \text{CbOF}_3 \cdot \text{H}_2\text{O}$ , gave first a white hydrate, then beneath the outer edge of the anode appeared a dark brown ring which gradually grew in toward the centre of the dish, never reaching it however, but stopping when about half an inch in width.

This brown substance was slightly adherent to the dish, but just as soon as the current was broken, and the liquid poured off, it reverted to the white hydrate. This change was so rapid that it was impossible to separate the brown from the white substance.

Thinking that this brown compound might be a contaminating element, about one gram of the double salt was dissolved in water and electrolyzed until the brown ring had appeared. Then the liquid was poured into another dish as quickly as possible, and the current run through again. The brown ring appeared as before, and was treated in the same manner. After changing the dish four times only a trace of brown could be seen. When the remaining solution was evaporated it was found that almost the entire quantity of the columbium had been precipitated. The brown substance here formed resembles in its behavior that produced in a like solution by zinc and hydrochloric acid.

The resistance of this solution is very high.

5. Potassium tantalum fluoride in aqueous solution was subjected to the action of a current of two amperes for six hours. A small quantity of hydrate was found in the liquid and on the dish a very slight iridescent deposit mixed with some white hydrate.

6. Potassium titanium fluoride was treated in the same manner as the previous salt. A small quantity of hydrate was found here, some of which adhered to the dish. The iridescent deposit, however, was wanting.

ACTION OF HYDROFLUORIC ACID UPON THE OXIDES OF TANTALUM, COLUMBIUM, TITANIUM, AND SILICON.

The well known volatility of the oxides of tantalum and columbium when heated with hydrofluoric acid led to the hope that in this behavior might lie a separation from titanium and also from silica.

Rose states that a very appreciable loss occurs when the first two oxides are treated as suggested, but he makes no attempt to separate them from the latter two. To this end one gram of the mixed oxides of tantalum and columbium was evaporated to dryness with hydrofluoric acid, the residue being heated over the free flame for a few minutes. By this treatment dense white vapors were driven off. Upon weighing the residual oxides they were found to equal 0.5464 gram. A second evaporation gave further loss, but as both columbium and tantalum continued to remain, the method is without value.

The separation of silica from these oxides can be accomplished by the heat of an iron plate after evaporating to dryness on a water bath. The final heating must be carefully done, and the acid should not be in too great excess.

I have never found it impossible to dissolve either the mixed or the pure oxide in hydrofluoric acid, even though strongly ignited. It is true, concentrated acid is necessary, and a little time is often required, but a perfect solution does take place.

Tantallic oxide, containing columbic oxide, is far more soluble in hydrofluoric acid than the pure oxide. The same behavior has been observed with pure columbic oxide, though it is not so pronounced as with tantallic oxide. Titanium dioxide, ignited, is very difficultly soluble in this reagent, though columbic oxide, containing titanic oxide, went quickly into solution.

DOUBLE FLUORIDES OF TANTALUM, COLUMBIUM, AND TITANIUM, WITH RUBIDIUM AND CESIUM.

The potassium double fluorides of tantalum and columbium have been found of great service in separating these two metals. Marignac first showed that a separation could be effected through these salts, and he also demonstrated that the sodium and ammonium salts were inapplicable.

Of the potassium double fluorides of tantalum and columbium we possess considerable information. A number have been isolated and studied. The sodium salts crystallize so poorly that their history is not so well known. It seemed probable that rubidium and cesium would form double fluorides of definite crystalline character with these three metals. At least, a study of their behavior might be found instructive. Before taking up their preparation, however, the simple fluorides of rubidium and cesium may be discussed.

*Rubidium Fluoride* (RbF). An examination of the literature on rubidium showed that its fluoride had not been prepared. In order to procure this, rubidium iodide was dissolved in water and moist silver oxide added to precipitate the iodine. The solution of rubidium hydrate resulting, was filtered off and evaporated in porcelain dishes. A very appreciable quantity of silver oxide was held in solution by the rubidium hydroxide, so that it was necessary to evaporate it almost to dryness, then to take it up in the smallest possible quantity of water and filter. This treatment may have to be repeated two or three times before the solution is perfectly colorless. When quite free from silver, the concentrated solution was made slightly acid with hydrofluoric acid, and evaporated. If hydrofluoric acid be present it is almost impossible to obtain crystals, a thick syrup being formed which defies all attempts in this direction. The solution is therefore evaporated with water several times until the excess of acid is expelled. The rubidium fluoride then crystallizes in long, transparent plates. These were drained, and dried between filter paper. The salt was anhydrous. Conversion into sulphate by evaporating with sulphuric acid gave, from 0.5 gram of the salt, 0.5236 gram rubidium sulphate. This corresponds, therefore, to the formula RbF.

*Cesium Fluoride*.—Cesium chloride was dissolved in water, and the chlorine precipitated by moist silver oxide. The solubility of the oxide of silver in cesium hydrate is even greater than in rubidium hydrate, therefore some difficulty was experienced in obtaining a hydrate free from silver. It was finally accomplished by evaporating to dryness repeatedly, taking up the cesium hydrate in a very small quantity of water and filter-

ing it. The pure hydrate was then neutralized with hydrofluoric acid and evaporated. A thick syrup was obtained, which refused to crystallize. Upon heating in an air bath to  $130^{\circ}\text{C.}$ , a crystalline mass formed, but it was always in such a sticky condition, and absorbed moisture so rapidly, that it could not be analyzed satisfactorily. This mass was dissolved in water and added to the solutions of the metals in hydrofluoric acid.

*Double Fluoride of Columbium and Rubidium.*—One-half gram of columbic oxide was dissolved in hydrofluoric acid and the calculated quantity of rubidium fluoride added. The solution was evaporated on a water bath to expel the excess of acid. The residue was taken up in hot water and allowed to crystallize spontaneously. White microscopic plates separated. These were filtered off, dried between filter paper, and analyzed. Two-tenths gram of the dry salt gave

	Found.	Calculated for $2\text{RbF.CbF}_6$ .	Difference.
$\text{Cb}_2\text{O}_3$ .....	0.0670	0.0673	—0.0003
$\text{RbF}$ .....	0.1048	0.1049	—0.0001

The formula of the salt is therefore,  $2\text{RbF.CbF}_6$ , corresponding to the tantalum salt usually obtained with potassium fluoride.

The filtrate from this first crop of crystals was slightly concentrated, when small, shining, or even iridescent crystals, apparently plates, separated. Upon standing a short time these changed over into crystals like those first mentioned. This salt is very soluble in water containing hydrofluoric acid, and also in pure water. It is insoluble in alcohol.

*Double Fluoride of Rubidium and Tantalum.*—Rubidium fluoride in slight excess was added to tantalic oxide dissolved in hydrofluoric acid. Small white needles crystallized out. An excess of acid must be present, otherwise heat decomposes the double salt, giving a fine, white, insoluble compound, as is the case with the potassium salt.

Analysis of two-tenths gram gave

	Found.	Calculated for $2\text{RbF.TaF}_5$ .	Difference.
$\text{Ta}_2\text{O}_5$ .....	0.0915	0.0913	+0.0002
$\text{RbF}$ .....	0.0861	0.0859	+0.0002

*Double Fluoride of Titanium and Rubidium.*—The preparation

of this salt was conducted as described with preceding salts. The crystals here were also microscopic needles. Some difficulty was at first experienced in completely drying the salt, but this was overcome by several recrystallizations from pure water, when an anhydrous product was obtained. One-tenth gram of the salt gave on analysis

	Found. Gram.	Calculated for $2\text{RbF} \cdot \text{TiF}_6$ Gram.	Difference.
$\text{TiO}_2$ .....	0.0238	0.0240	—0.0002
$\text{RbF}$ .....	0.0622	0.0626	—0.0004

*Double Fluoride of Tantalum and Cesium*<sup>1</sup>.—This double salt was formed by the addition of a solution of the cesium hydrate in hydrofluoric acid to a solution of tantalic oxide in hydrofluoric acid. Very beautiful white needles separated, which were not easily soluble in water, and were not decomposed by recrystallization from pure water. The aqueous solution may be evaporated on a water-bath with perfect safety, this salt being apparently much more stable than either the potassium or rubidium salt.

The crystals were dried in the air, then heated to  $125^\circ \text{C}$ . in an air-bath. No loss in weight was observed. 0.25 gram gave on analysis

	Found.	Calculated for $15\text{CsF} \cdot \text{TaF}_6$	Difference.
$\text{Ta}_2\text{O}_5$ .....	0.0212	0.0217	—0.0005
$\text{CsF}$ .....	0.2232	0.2228	—0.0004

The formula deduced from the analytical data varies widely from that generally followed by tantalum double fluorides. Neither is it in accordance with Remsen's law for the double halides<sup>2</sup> though it will be observed that its fluorine content bears a simple ratio to the fluorine in combination with the tantalum.

*Double Fluoride of Columbium and Cesium*.—This double salt was formed in the manner described for the preparation of the cesium tantalum fluoride. It is very soluble in water containing hydrofluoric acid, and in pure water, from which it crystallizes in needles. These when pure are anhydrous. Boiling

<sup>1</sup> This and all the other cesium double fluorides are being subjected, at this writing, to further study in this laboratory.

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<sup>2</sup> *Am. Chem. J.*, 2, 291.

with pure water does not decompose the salt. Analysis of two-tenths gram gave the following result :

	Found.	Calculated for $7\text{CsF.CbF}_6$ .	Difference.
$\text{Cb}_2\text{O}_3$ .....	0.0216	0.0213	+0.0003
$\text{CsF}$ .....	0.1694	0.1698	-0.0004

This salt, which appears to be  $7\text{CsF.CbF}_6$ , is even more erratic in its constitution than the tantalum cesium compound. There is apparently no relation here between the fluorine in combination with the columbium and the number of molecules of cesium fluoride present.

*Double Fluoride of Titanium and Cesium.*—This salt separates in very small shining crystals when cesium fluoride is added to a rather concentrated solution of titanic oxide in hydrofluoric acid. It is more readily soluble in water than the tantalum cesium compound, and is not decomposed by pure water. The air dried crystals showed no loss in weight after heating for some time at  $125^\circ\text{C}$ . An analysis of 0.25 gram gave the following amounts of titanic oxide and cesium fluoride :

	Found.	Calculated for $4\text{CsF.TiF}_4$ .	Difference.
$\text{TiO}_2$ .....	0.0269	0.0271	+0.0002
$\text{CsF}$ .....	0.2071	0.2076	-0.0005

The figures point to the formula  $4\text{CsF.TiF}_4$ . This is a departure from the usual titanium double fluorides, and agrees with the law laid down by Remsen for these salts.

When we consider the atomic masses of tantalum, columbium, and titanium, the first 182, the second 94, and the third 48, and also consider the quantities of cesium fluoride which unite with a molecule of each of the metallic fluorides, we find that with tantalum the quantity (fifteen) is nearly twice that with columbium (seven) and the latter almost double that (four) uniting with titanium, just as 182 is about twice 94, and 94 nearly twice 48.

These new cesium compounds tend to confirm the conclusions drawn by Wells and others<sup>1</sup> from their work on the cesium double halides. The compounds investigated by these chemists show that the cesium double halides are not wholly conformable to Remsen's law.

<sup>1</sup> *Am. J. Sci.* 47.

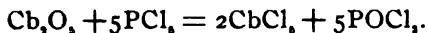


The method of analysis pursued for the determination of these double salts is, briefly, as follows :

The dry substance was decomposed in a platinum crucible by a few drops of concentrated sulphuric acid. The hydrofluoric acid was driven off, and the excess of sulphuric acid was then expelled on a sand-bath. The temperature must be just sufficient to drive off the acid. The metallic oxide was obtained from the sulphate by long boiling with a large quantity of water. It was then filtered, washed about twenty times with boiling water, ignited, and weighed. The filtrate, containing the alkaline sulphate, was evaporated, the excess of acid neutralized with ammonium carbonate, and the solution then evaporated to dryness on a water-bath. A saturated solution of ammonium carbonate was added, and the mixture evaporated again to dryness. The ammonium salts were expelled by careful heating. Constant weight can generally be obtained after two or three evaporations with ammonium carbonate. The rubidium sulphate decrepitates on heating, which necessitated great care while expelling ammonium salts, and also rendered the method proposed by Krüss (heating in a stream of ammonia gas), untrustworthy. The alkalies were then weighed as normal sulphate, and the cesium or rubidium content calculated. This method, while slow, has been found very satisfactory for these rare alkalies.

**PRODUCTS OBTAINED ON HEATING THE OXIDES OF TANTALUM AND COLUMBIUM WITH PHOSPHORUS PENTACHLORIDE.**

One-half gram of columbic oxide was heated with phosphorus pentachloride, the quantity being calculated from the following equation :



The experiment was conducted in a sealed tube from which all air had been expelled, the temperature being maintained at  $180^\circ$ – $200^\circ$  C., for seven hours. The resulting mass was moist, and a dirty green. The tube was opened, connected quickly with a small test tube, and then heated in an air-bath. A small quantity of liquid distilled into the front part of the tube. This was a yellowish green, and gave with water a white precipitate, apparently a hydrated columbic oxide.

At a higher temperature, about  $200^{\circ}$  C., yellow vapors collected in the cool portion of the tube. These settled on the glass as yellow, oily drops, and on cooling solidified, long yellow needles being detected here and there. Nearly all of the substance in the tube, however, remained as the greenish mass, which had become dry. No change was observed on heating above  $360^{\circ}$  C. The tube was then wrapped in copper gauze and heated with a Bunsen lamp. The green substance swelled up, became white, iridescent, and almost filled the tube. No green color remained. Analysis of this compound showed it to be columbium oxychloride,  $\text{CbOCl}_2$ . The long yellow needles which had been observed in the front part of the tube changed gradually on heating, and became white and iridescent like the remainder of the substance.

This behavior indicated the formation of a pentachloride, which was then changed to oxychloride by the small quantity of air which entered the tube when it was connected with the receiver.

A second tube, heated for eight hours at  $230^{\circ}$ – $235^{\circ}$  C., gave a dark yellow, semi-fluid mass. Great care was taken in this experiment to exclude all traces of moisture, and the distillation was conducted under reduced pressure. Phosphorus oxychloride in considerable quantity distilled over, leaving in the tube a yellow crystalline substance which, on treating with water, decomposed with hissing and an evolution of hydrochloric acid gas. This compound was analyzed according to the method of Margner. The dried oxide weighed 0.542 gram. As only one-half gram of columbic oxide was used in the experiment the contaminating substance was slight and was found to be phosphorus. Two moles of lime were necessary for the extraction of the excess. Phosphoric acid was also present in the residue from the peroxide.

The results of the analysis of the powder of this phosphorus compound is given in a compound termed containing columbium, phosphorus and oxygen. It is the phosphorus content due to the phosphorus pentachloride in the excess of phosphorus pentachloride.

1898, 1899, 1900.

Another experiment was therefore tried under the following conditions: One-half gram columbium pentoxide was heated with the calculated quantity of phosphorus pentachloride at a temperature not exceeding  $210^{\circ}$  C. for eight hours. The tube contained a yellow mass as before. It was placed in an air-bath and connected with a chlorine generator, the receiver having been previously filled with chlorine. At  $190^{\circ}$  C. a very volatile substance collected in the front part of the receiver. This was a lemon yellow, and when analyzed gave 15.85 per cent. columbium and 6.095 per cent. phosphorus.

At  $190^{\circ}$ – $200^{\circ}$  C., long yellow needles collected; some of these were nearly half an inch in length. Analysis gave 27.37 per cent. columbium and 32.19 per cent. phosphorus.

The substance which did not volatilize at  $200^{\circ}$  C. was brownish-yellow, and apparently crystalline. Analysis gave 28.11 per cent. columbium, and 1.34 per cent. phosphorus.

In none of these analyses could the chlorine content be determined, because of the violence with which water acts upon the compounds, resulting invariably in the loss of some hydrochloric acid.

It seemed probable that the brownish-yellow residue in the tube was columbium pentachloride, enclosing a small quantity of phosphorus pentachloride. To determine all three elements, the following method was used:

The more volatile compounds having been removed by distillation in a stream of chlorine gas the residual substance was quickly weighed and thrown into a dilute solution of silver nitrate. The precipitate of silver chloride, silver phosphate, and hydrated columbic oxide was then filtered, and washed on the filter with dilute nitric acid. The phosphoric acid obtained was determined by a magnesium mixture. Dilute ammonium hydroxide was then poured over the mixture of silver chloride and columbic oxide. It was found that all the silver salt could not be removed by this means. The mixture was therefore transferred to a porcelain crucible and reduced in a stream of hydrogen gas, the metallic silver being dissolved out with dilute nitric acid, then precipitated as chloride. The columbium remained

in the form of a violet compound, which on ignition in the air went over to pentoxide.

A small quantity of phosphorus was obtained, which was calculated into pentachloride and deducted from the material taken.

Rose states that a columbate of silver,  $\text{Cb}_2\text{O}_5 \cdot \text{Ag}_2\text{O}$ , is formed on the addition of silver nitrate to a solution of sodium columbate. As, upon the addition of water to columbium pentachloride, an almost perfect solution is produced for a few moments, the columbium in solution may combine with the silver. In such a case the silver chloride finally weighed would represent both the silver in combination with chlorine and that with columbium.

The analytical results are as follows:

Substance taken = 0.8017 gram.

Phosphorus found = 0.02590 gram.

This, as phosphorus pentachloride, requires 0.14829 gram of chlorine.

Substance taken minus  $\text{PCl}_5$  = 0.7175 gram.

Columbium found = 0.2185 gram.

Columbium required = 0.2184 gram.

Chlorine found = 0.06500 gram.

Taking from this 0.14829 gram of chlorine, which is in combination with phosphorus, we have chlorine = 0.5168 gram; columbium pentachloride requires 0.4001 gram. Calculating the quantity of silver which, according to Rose's formula, would combine with the amount of columbium oxide found, and deducting the chlorine corresponding to it, 0.1690 gram of chlorine is found to be in combination with the columbium.

The volatile compounds mentioned above were recalculated into phosphorus pentachloride and columbium pentachloride. It was found that by removing the phosphorus as pentachloride satisfactory analyses for columbium pentachloride were obtained from the residues.

*Tritium acid* was also heated with phosphorus pentachloride, the same conditions being maintained as in the columbium experiments. A yellow mass was formed lighter in color than the columbium compound and only slightly moist. The tube was placed in an airbath and distilled at a temperature not exceeding  $125^\circ \text{C}$ . This distillation was conducted under

reduced pressure. A small quantity of phosphorus oxychloride distilled over, and in the front part of the tube a little phosphorus pentachloride collected. The tantalum compound remaining was light yellow, dry, and powdery—apparently amorphous. It combined with water with hissing, liberating tantalic oxide, which contained no phosphorus. A small quantity of this element was found in the filtrate from the oxide. It was calculated into phosphorus pentachloride, and deducted from the total quantity.

Weight of substance taken = 0.6700 gram.

Weight of tantalum found = 0.3389 gram.

Required tantalum = 0.3391 gram.

Tantalum pentachloride is, therefore, formed when tantalic oxide is heated with phosphorus as pentachloride.

#### REDUCTION OF THE COMPOUNDS OF COLUMBIUM AND TANTALUM TO METAL.

Two experiments aiming at the preparation of columbium and tantalum in the metallic state have been tried during this research, and I regret exceedingly that lack of time has prevented a more careful study of the reactions obtained. It is my intention to go more deeply into the subject than I have been able to do.

*Experiment 1.* An iron cylinder, three inches in diameter, having an inch bore, was charged in the following manner: First, a layer of dry salt, then a layer of metallic sodium, above which were placed about seven grams of potassium tantalum fluoride, this being followed by another layer of sodium. The cylinder was then tightly packed with dry salt, and a heavy lid screwed on. It was then placed in a wind furnace, the temperature of which was comparatively low. In less than one-half hour it was found that the cylinder had melted down, and no trace of the charge could be found.

*Experiment 2.* Marignac obtained an alloy of columbium and aluminum by heating the potassium double fluoride with aluminum scales in a carbon crucible. In the experiment to be described columbic oxide was used, salt and cryolite being employed as a flux. The following layers were placed in a graphite crucible:

1. Salt.
2. Cryolite.
3. Aluminum clippings.
4. Columbic oxide.
5. Aluminum clippings.
6. Cryolite.
7. Salt.

The proportion of these substances used were :

- 2 parts  $\text{Cb}_2\text{O}_3$ .
- 10 parts cryolite.
- 15 parts aluminum.
- x parts sodium chloride.

The graphite lid was firmly luted on with fire-clay, the crucible was buried in a wind furnace which was kept at a white heat for eight hours. At the end of this time it was found that the graphite crucible had been severely attacked. It was reduced to a shapeless mass, but on breaking, a powdery substance was found, in which were contained many little metallic buttons varying in size from a large pea to those of microscopic proportions. These were carefully picked out, and various reagents tried upon them.

Single acids do not attack them. Aqua regia makes a slight impression on long heating. Fusion with bisulphate affords only a partial decomposition. The substance is exceedingly light, it is dark gray, and does not alter in the air. A partial oxidation occurs after prolonged heating in the air. The substance is not brittle.

#### SUMMARY.

1. The decomposition of columbite is more readily and satisfactorily accomplished by the Gibbs than by the bisulphate method. This method is also more valuable for the preparation of large quantities of pure oxides.
2. The qualitative reactions of columbium, tantalum and titanium when existing as double fluorides are not the same as when the metals exist as tantalates, columbates and titanates.
3. The action of the electric current upon tantalum and columbium double fluorides gives a lower hydrated oxide. The precipitation is not complete.
4. It was hoped that in preparing the double fluorides of

columbium, tantalum and titanium with rubidium and cesium a difference in solubility of the salts would be found which would afford a better separation of these metallic oxides under discussion. This hope has not been realized.

5. Heating the oxides of columbium and tantalum in sealed and vacuous tubes with phosphorus pentachloride yields the pentachlorides of these metals and phosphorus oxychloride.

I take pleasure in acknowledging the kindness shown, and the interest taken in the preceding work by Dr. Edgar F. Smith, of this University, in whose laboratory it was carried out.

UNIVERSITY OF PENNSYLVANIA,  
JUNE, 1895.

## AN IMPROVED GAS PIPETTE FOR THE ABSORPTION OF ILLUMINANTS.

BY AUGUSTUS H. GILL.

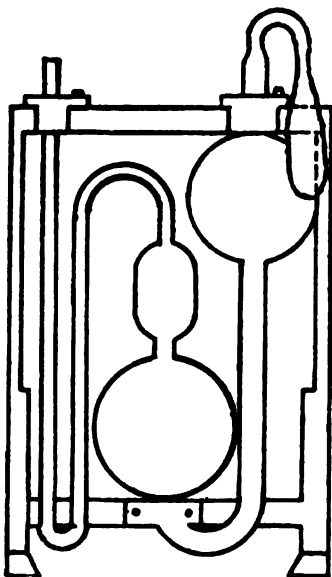
Received October 12, 1895.

IN the use of the apparatus for this purpose ordinarily furnished by the dealers, difficulty has always been experienced in sucking the gas back from the pipette, owing to the moist beads and the glass wool entrapping some bubbles.

To obviate this, the writer has, for the past two years, made use of the modification shown at one-fourth size in the sketch. The round bulb filled with beads and glass wool in the usual form, is replaced by a cylindrical one about two inches long and an inch and a quarter in diameter, filled with tubes standing vertically, after the manner of the Orsat pipettes. The surface presented is nearly the same and no trapping of the gas can take place.

The stand is the one already described,<sup>1</sup> and the whole apparatus may be obtained of the Ziegeler Electric Co., of Boston.

<sup>1</sup> Gill: *Am. Chem. J.*, 14, 231.



## THE COLORING-MATTER OF NATURAL WATERS, ITS SOURCE, COMPOSITION AND QUANTITATIVE MEASUREMENT.

BY ELLEN H. RICHARDS AND J. W. ELLMS.

Received August 31, 1895.

SO deeply seated in the mind of the average citizen is the prejudice against the amber-colored water of the most of the New England streams that it is only when reinforced by scientific authority that water boards and city councils are able to make any impression upon it.

It is only by actually filling up the well or by taking out the pump, that any Board of Health can prevent the use of a clear, cold, colorless, highly polluted well-water, no matter how abundant and free the tepid, turbid brown water supplied from the tap.

Color seems to have been associated in the popular mind with all sorts of hidden dangers. There lingers yet in memory the echoes of stories told to childish ears of the agonies suffered by those deluded persons who, in spite of the warning of their elders, persisted in drinking from wayside brooks and thus unwittingly swallowed what grew to be living monsters within them.

While there must be some ground for so strong and universal a feeling of danger, experience has certainly shown that a brown water from a carefully protected water-shed, when properly stored, yields a perfectly wholesome as well as most available and abundant source of supply.

It is said that the water from the Dismal Swamp is sought for by sailing vessels to take for three year cruises and many other brown waters have shown excellent keeping qualities after being stored for a time in clean basins to allow of the sedimentation of the extraneous matter which may have been carried along by streams.

The source of brown color in natural surface waters is to be found in the decaying elm, maple, oak, and other leaves which carpet the hillsides and swamps each autumn, and in the surface soil, which everywhere, and particularly in the lowlands, is rich in peaty or "humus" matter.



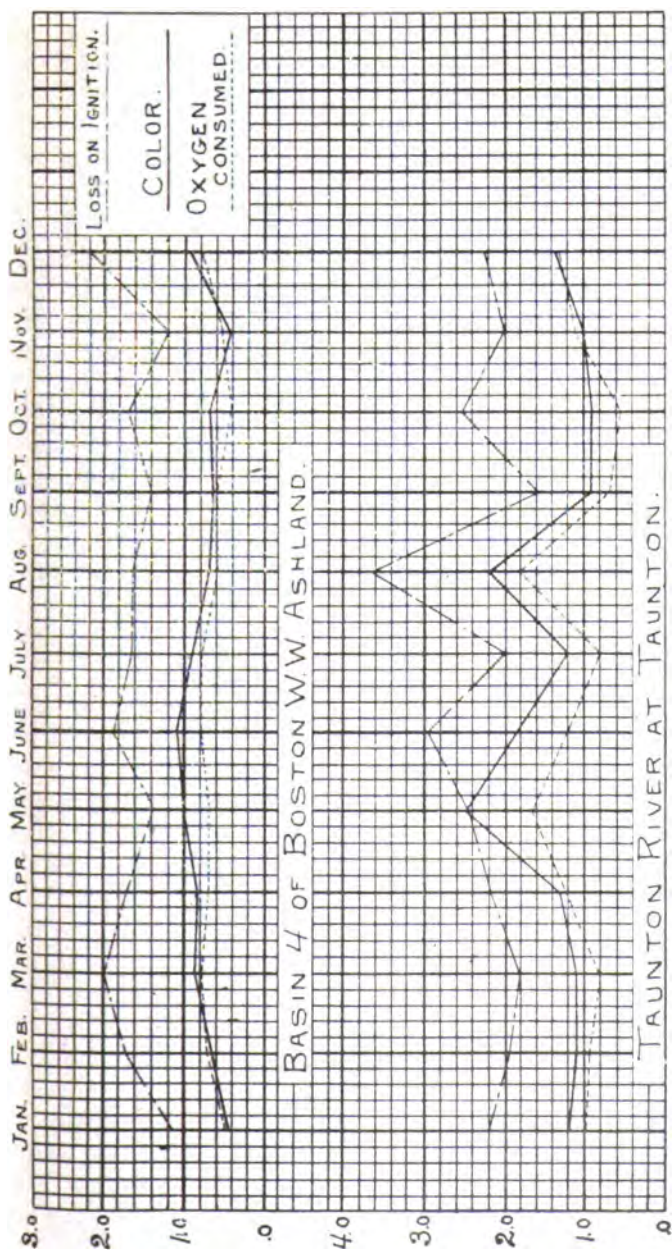


CHART I.

The chlorophyl derivatives, glucoses, and glucosides dissolve out of the fallen leaves in the early autumn, giving a light yellow color to the brooks, but after soaking all winter, mostly under the ice and snow, the leaves yield to the warm spring rains a rich deep brown liquid which is exactly what Thoreau, with poetic instinct, called it, namely "meadow tea." It is at least as harmless as Japan tea. The coloring-matter in both cases is due to the slow carbonizing of the leaf and the formation of soluble compounds rich in carbon.

The variation in the depth of color of brown surface water at different seasons of the year, is well shown in chart 1. The color curve plotted for basin 4 of the Boston Water Works, in Ashland, for a year, shows the steady rise in color from January to June, and then a falling off toward the latter part of the year. This is a typical, unpolluted surface water. Taunton river, on the other hand, receives drainage from a variety of sources as well as from the neighboring swamps, and shows greater fluctuations.

When any organic substance as wood, leaves, and the like, is treated with strong sulphuric acid, a decomposition occurs more or less complete; and the result is, according to the strength of the acid and the temperature at which it is applied, either a mass of nearly pure carbon or a gummy substance soluble in water with the production of a deep brown-colored solution. When sugar is gently heated it parts with a portion of the elements of water, becoming richer in carbon as the process is pushed farther. The result is a brown substance known as "caramel" soluble in water; there also may be produced various less soluble compounds, depending on the temperature used, which have been at times called caramelane, caramelin, and caramelene.<sup>1</sup>

But the most instructive instance of the production of this characteristic brown substance is, perhaps, in the case of the well known colorimetric determination of carbon in steel. By using Stead's alkali method, a soluble brown color is obtained which compares very closely with the color of the dark brown waters under consideration. Whether an estimation of the

<sup>1</sup> Peligot, *Ann. chim. phys.* [2], 67, 172; Völckel, *Ann. Chem.* (Liebig), 85, 59; Maumené, *Compt. rend.*, 39, 422; Graham, *J. Chem. Soc.*, 15, 258.

actual quantity of carbon in these coloring-matters can be made, is yet to be determined.

The color in solutions from all these sources may be removed with milk of alumina, may be precipitated by barium hydroxide, and in all cases the solutions are decolorized by the action of potassium permanganate, indicating the complete oxidation of the color-giving compound of carbon. All are comparable in color when matched in tubes or read in the tintometer to be described.

These facts all indicate that this brown color is imparted to aqueous solutions by the same compound of carbon or by closely related compounds.

In the coloring-matter of surface waters there are, most probably, several complex substances, among them tannins, glucosides, and their derivatives, out of which it seems almost hopeless to attempt to isolate any one which may be said to be the substance under consideration. Some of these decomposition-products contain iron and it has been suggested that the color-giving compounds may result from the breaking up of chlorophyll.<sup>1</sup> That iron is not essential to the formation of the color is shown by the fact that the brown color may be given by a solution of caramel made from pure sugar, and that iron may be absent from the carbon color obtained from steel, but it is true that a very small quantity of iron does, as a rule, accompany the brown color of natural waters.

Since any colored natural water gives a certain proportion of albuminoid ammonia, increasing as the color increases, it would seem that the color compound might contain nitrogen. The following are results of experiments tried some years ago :

	Color.	Albuminoid ammonia.
(1) Peat solution .....	2.0	0.0516
(2) Fresh leaf solution.....	0.8	0.0494
(3) Second extract of same leaf .....	0.8	0.0174
(4) An old leaf repeatedly extracted with water.....	0.9	0.0072

It will be seen in the two leaf solutions (2 and 3) with the same color of eight-tenths there is a reduction of 64.7 per cent. in the nitrogen and that with a color of one-tenth more in the

<sup>1</sup> F. S. Hollis, Report of the Boston Water Board, 1892.

old leaf solution (4) there is 85.4 per cent. less nitrogen than in the fresh leaf solution (2). While it is possible that the color-giving compound or compounds contain nitrogen as an essential constituent, it is evident that a large diminution in the nitrogen does not produce a corresponding lessening of the color.

The following figures show the carbon, hydrogen, and nitrogen contained in (1) the residue of Boston tap water, (2) a very dark-colored water from Cedar Swamp, Westboro, and (3) humic acid extracted from soil.

	Carbon.	Hydrogen.	Nitrogen.
Boston tap water <sup>1</sup> .....	30.71	5.96	7.68
Cedar Swamp water <sup>1</sup> .....	43.72	3.92	4.82
Humic acid <sup>2</sup> .....	50.4	4.8	3.6

No attempt has been made by us to give a more definite formula for these apparently highly carbonaceous compounds since so little seems to be known of the reactions attending the gradual carbonization of such organic substances. It is probable that one of the compounds may be what is known to the agricultural chemist as humic acid or humus matter. Berthelot finds a close relation between this substance prepared from peat and from sugar, only the latter is free from nitrogen.

#### QUANTITATIVE MEASUREMENT.

Formerly the brown color of water was supposed to be a bar to its use for domestic purposes and analysts sought for some standard of comparison by which to set a limit of allowable color. One of the early methods was by the determination of the quantity of oxygen consumed or absorbed from potassium permanganate, either hot or cold in acid or alkaline solution. If the substance which gave the brown color had a known composition so that any given percentage of oxygen consumed could be said to correspond to a definite quantity of the carbonaceous compound, this might be a valuable standard. The fact is, however, that at present the results are often misleading, since a highly polluted water may give much lower results than a dark brown water which by years of use has been shown to be perfectly wholesome.

<sup>1</sup> H. T. Gallup, Thesis, Mass. Inst. Tech., 1894.

<sup>2</sup> Berthelot: *Compt. rend.*, 569 1892.

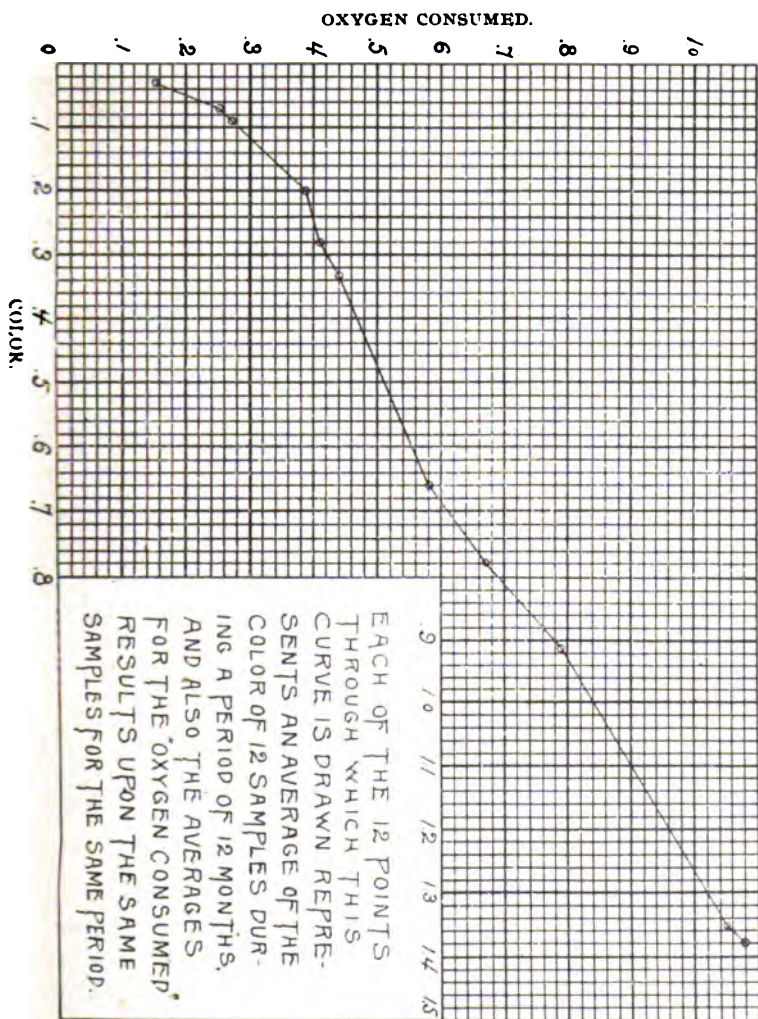


CHART II.

Since not all carbon compounds are affected by this treatment and since the organic matter in solution is probably made up of several substances having quite different composition, it is not surprising that we have thus far failed to establish a definite relation between the quantity of organic matter present and the oxygen given up to it by the potassium permanganate. In a

general way, a rise in color is followed by a rise in the oxygen consumed, as is shown by the diagram on chart II.

As soon as the fact was recognized that fixed standards could not be rigidly applied to all waters from all sources, and that a certain quantity of albuminoid ammonia invariably accompanied the brown color of perfectly wholesome water and somewhat in proportion to the color,<sup>1</sup> it became of importance to be able to estimate the relative depth of color in waters. For this some standard was of course required. Various substances have been proposed from time to time, such as solutions of caramel, and metallic solutions<sup>2</sup> of various kinds. Largely on account of its convenience as being always in use in the laboratory and because the colors matched easily, the method originally suggested by Prof. A. R. Leeds,<sup>3</sup> namely, the use of the nesslerized ammonia standards, was at first adopted in the Laboratory for Water Analysis of the Institute of Technology.

It occurred to one of us to prepare considerable quantities of water of the various depths of color most frequently met with in ordinary routine work, and to use these as standards of comparison, of course based upon the ammonia standards made with a Nessler solution which gave a sufficiently brown tint. An additional advantage to that of having them ready at a moment's notice was that the colors were identical and no mental effort was necessary to eliminate the slight differences in tint which almost of necessity occurs when two substances of unlike composition are compared.

Natural water standards when so prepared fade in time like the caramel solutions, even when carefully covered from the light, and, although sterilized at first, the bottles cannot remain so when opened for daily use, so that a freshly standardized set is required as often as once in six months. It is well known that the Nesslerized ammonia standards vary considerably as prepared in different laboratories because of the different methods of making up the Nessler solution, and it was very desirable

<sup>1</sup> T. M. Drown. The Interpretation of Analyses, Mass. State Board of Health Report, 1890, p. 566.

<sup>2</sup> Crookes, Odling & Tidy. *Chem. News*, 43, 174; Hazen; *Am. Chem. J.*, 14, 300.

<sup>3</sup> Proceedings Am. Chem. Soc., 2, 8.

<sup>4</sup> Mrs. E. H. Richards, Mass. State Board of Health Report, 1890, p. 532.

to find some standards of absolute quantitative value, which could be applied anywhere, and which would give comparable results.

Many chemists have found the metallic standard of platinum and cobalt satisfactory for tests for the working of filters and where only low colors are dealt with; but for the wide range of colors met with in our work, some 500 numbers from 0.01 to 5.00, we cannot match two such different combinations of colors with any degree of accuracy in the higher portions of the scale.

The reason is evident, and it is equally patent in all forms of color measurement; "for color is not a simple physical quantity like weight or temperature, but a physiological effect which varies with individual peculiarities and bears no very simple relation to the physical causes which produce it."<sup>1</sup>

The constituents of the resulting matched colors also may be very different and one may vary more than the other under varying conditions of light, depth of column, and density.

There is a wide field for experiment in the physics of color-measurement in solution and which in view of the increasing use of such methods in quantitative determinations is of extreme importance to chemists. Without going into detail on this point, one instance may be cited. It has been observed in matching Nessler standards that the readings are exact only within certain limits; for instance, colors higher than those given by four cc. of standard ammonia, 0.00001 gram in one cc. observed in a column of nine inches in depth, are very difficult to compare, and as the quantity of ammonia increases the color becomes more and more red until the point of precipitation is reached. That is, the normal eye is more sensitive to certain shades of color than to others and there is a limit to the depth of color which can be correctly estimated. Also, while one solution may appear redder than another in a deep column it may appear less red in another of a less depth. For example, a natural water standard of color, 5.0 on the Nessler scale contains only 0.0005 per cent. dissolved organic matter. A solution of carbon from steel, prepared by Stead's<sup>2</sup> method, is

<sup>1</sup> H. R. Proctor: *J. Soc. Chem. Ind.*, 14, 2.

<sup>2</sup> *J. Iron and Steel Inst.*, 1883, p. 213; also Blair's *Iron Analysis*, p. 170.

strongly alkaline and contains twenty per cent. dissolved salts. A solution of caramel is nearly the same in character as the water, and a strongly acid solution of platinum and cobalt contains two-tenths per cent. of salts. If these solutions are matched as nearly as possible by the eye in nine-inch tubes and then the tintometer readings are taken, it is found that the ratio of orange to excess of yellow in the water standard is as one to 1.21, or the color is yellow orange.

The ratio in the solution of the carbon from steel is one to 1.38, or a slightly yellower orange; the ratio in the caramel is one to 1.42, while in the platinum cobalt it is one to 1.6, or a decidedly yellow orange.

It will be evident therefore, why an optical instrument of precision which promised to furnish a universal standard applicable anywhere, was eagerly welcomed.

The tintometer devised by Joseph W. Lovibond, of Salisbury, England, was examined by Dr. T. M. Drown in the inventors laboratory, and an instrument was imported for the use of the State Board of Health.

It consists of two tubes side by side with openings at one end and divided by a central taper partition terminating with a knife edge at the eye piece, which it divides equally in such a way that on looking through the eye piece the two openings are simultaneously visible. The liquid is placed in cells of definite lengths, one inch, two inches, up to twenty-four inches. The standards consist of three sets of graded colored glasses, red, yellow and blue, numbered according to their depth of color.

"By using several superimposed glasses from a set, a depth of color is represented by the aggregate of tint number on the glasses used, whilst glasses from different sets produce a composite color, and the exact proportion of each component color can be read off."

The use of the Lovibond instrument in our hands has been confined first, to the determination of the color scale which has been in use for the past eight years in the laboratory for water analysis of the Institute of Technology, and by which the numbers found in the reports of the Mass. State Board of Health, in the tabulated result of 15,000 samples, have been obtained; and



secondly, to a color comparison of some other substances in order to find some standard by which a quantitative estimation of the carbon present may be made.

The natural water color standards are prepared by dilution of a highly colored surface water with distilled water. At certain points in the scale the dilution is such that when the colors are read in 50 cc. tubes they match Nesslerized ammonia (0.01 mg. ammonia per cc.) standards read in the same volume and depth (23.5 cm.) The points in the scale at which this matching is made are at 0.2, 0.5, 1.3, 1.8 and 2.0.

Above the color standard of 2.0 the scale is prepared by dilution of the highly colored water in such a manner as to have the quantity of color proportionate to the depth in which the reading is made. For example, a color of 4.0 is prepared so that when read in one-half the usual depth, (*i. e.*, 11.75 cm.) it matches a color of 2.0 read in the full depth (23.5 cm.).

From the color 0.00 (distilled water) up to 0.2, and for the intervals between the points matched against the Nesslerized ammonia standards, the gradation is made by the eye.

The standard colors to be measured by the tintometer were prepared in this way, and were read in four different lengths of cell. Colors from 0.00 in the scale to 0.3 inclusive, were read in a twenty-four inch cell, from 0.3 to 1.5 in a six inch cell, from 1.5 to 4.0 in a two-inch cell, and from 4.0 upwards in a one inch cell. This method permitted the readings for the "standard yellow glasses" to be kept within 4.0 of the tintometric scale. This is desirable for the reason that the eye is liable to be less sensitive in reading above 4.0 of the "yellow standard glasses" than below that limit.

The following condensed table (No. 1.) gives the readings of the laboratory standards. The measurements are tabulated for convenience in units of yellow, red and blue of the tintometric scale. It must be understood, however, that the color transmitted to the eye when red and yellow glasses alone are used, and when the number of units of yellow exceed those of the red, is orange mixed with yellow. If yellow and blue glasses are used together, the color transmitted is violet with a mixture of blue or yellow,

as the case may be, depending upon the preponderance of one or the other of those colors. A neutral tint unit is obtained by a combination of three equal color units. Therefore, if the three colors are used, black or a decrement of normal white light is obtained.

TABLE NO. I.

READINGS OF THE TINTOMETER "STANDARD GLASSES" FOR YELLOW, RED AND BLUE, WITH THE DIFFERENT LENGTHS OF CELLS USED.

	Natural water standard color scale.	Yellow.	Red.	Blue.	Yellow.	Red.	Yellow.	Red.	Yellow.	Red.
Section 1. Color of water measured in a cell 24 inches in length.	0.00	0.40		1.00						
	0.05	0.90		0.20						
	0.10	1.20	0.10							
	0.15	1.90	0.32							
	0.20	2.40	0.84							
	0.30	3.50	1.05		0.80	0.30				
Section 2. Color of water measured in a cell 6 inches in length.	0.40			1.10	0.42					
	0.50			1.35	0.58					
	0.60			1.60	0.66					
	0.70			1.85	0.80					
	0.90			2.40	1.10					
	1.00			2.70	1.25					
	1.20			3.20	1.55					
	1.30			3.50	1.70					
	1.50			3.90	1.85	1.20	0.60			
Section 3. Color of water measured in a cell 2 inches in length.	1.80					1.35	0.70			
	2.00					1.50	0.80			
	2.50					1.95	1.00			
	3.00					2.50	1.20			
	4.00					3.20	1.60	1.60	0.80	
Section 4. Color of water measured in a cell 1 inch in length.	5.00							1.95	1.00	

If the color sensations were transmitted uniformly, then, having obtained a reading in a given length of cell for a color of 0.2 a color of 0.6 would give three times as much yellow and three times as much red, and a color of 1.8 would give nine times as

much yellow and nine times as much red, but as a matter of fact the actual reading shows sixteen times as much yellow and eight and two-tenths times as much red.

The following table will show this more distinctly :

READING OF 0.2 COLOR IN TWENTY-FOUR INCH CELL, = 2.40 YELLOW, 0.80 RED.

		Calculated readings.		Observed readings.	
		Yellow.	Red.	Yellow.	Red.
Color.....	0.6	7.20	2.40	7.60	2.40
" .....	1.0	11.00	4.00	15.53	3.65
" .....	1.8	22.80	7.20	38.49	6.60

Therefore, in the case of a higher color a shorter length of cell is used, so that the readings may be always made with lighter colored glasses.

The second table (No. 2) represents the differences for each tenth of color in the natural water standard scale, beginning with 0.00 and running to 5.0, as measured by the tintometer "standard glasses" for both yellow and red. In one column is shown the estimated difference for yellow and red, if the increase in any section were proportional to the numerical increase of the natural water standard scale. The basis for calculation is arbitrary for each section. (The section here is the division made by reading in the different lengths of cell.) The basis of calculation for the first section (twenty-four inch cell) is the color standard (0.1) which reads yellow 1.20, red 0.10. For the six inch cell the color 0.3 which reads yellow 0.80, red 0.30. For the two inch cell, the color 0.5, which reads yellow 1.20, red 0.60, and for the one inch cell, the color 4.0 which reads yellow 1.6, red 0.80. It will be seen that the estimated and observed differences agree quite well and indicate a regular increment of color as the scale ascends.

Considering the fact that we have had the instrument in our hands for a few months only and that we have been able to give to it only the odds and ends of time which a full daily routine left at our disposal, and therefore, that we cannot claim to have as yet perfectly trained eyes, the results are very encouraging, especially as in the case under consideration, we have to deal with a mixture of very impure colors.

**TABLE NO. 2.**  
**DIFFERENCES IN THE TINTOMETRIC READINGS OF RED AND YELLOW**  
**FOR EACH TENTH OF COLOR IN THE NATURAL WATER**  
**STANDARD SCALE.**

	Natural water stand- ard color scale.	Yellow.	Red.	Estimated difference.
Sec. 1. Color of water measured in a twenty- four inch cell.	0.00			
	0.10	0.80		Yellow = 1.20
	0.20	1.20	0.74	Red = 0.10
	0.30	1.10	0.21	
Sec. 2. Color of water measured in a six inch cell.	0.40	0.30	0.12	
	0.50	0.25	0.16	
	0.60	0.25	0.08	
	0.70	0.25	0.14	
	0.80	0.275	0.15	
	0.90	0.275	0.15	
	1.00	0.30	0.15	Yellow = 0.27
	1.10	0.25	0.15	Red = 0.10
	1.20	0.25	0.15	
	1.30	0.30	0.15	
	1.40	0.20	0.075	
	1.50	0.20	0.075	
	1.60	0.05	0.033	
	1.70	0.05	0.033	
Sec. 3. Color of water measured in a two inch cell.	1.80	0.05	0.033	
	1.90	0.075	0.05	
	2.00	0.075	0.05	
	2.10	0.09	0.04	
	2.20	0.09	0.04	
	2.30	0.09	0.04	
	2.40	0.09	0.04	
	2.50	0.09	0.04	
	2.60	0.11	0.04	Yellow = 0.08
	2.70	0.11	0.04	Red = 0.04
	2.80	0.11	0.04	
	2.90	0.11	0.04	
	3.00	0.11	0.04	
	3.10	0.07	0.04	
	3.20	0.07	0.04	
	3.30	0.07	0.04	
	3.40	0.07	0.04	
Sec. 4. Color of water mea- sured in a one inch cell.	3.50	0.07	0.04	
	3.60	0.07	0.04	
	3.70	0.07	0.04	
	3.80	0.07	0.04	
	3.90	0.07	0.04	
	4.00	0.07	0.04	
	4.10	0.035	0.02	
	4.20	0.035	0.02	
	4.30	0.035	0.02	
	4.40	0.035	0.02	
	4.50	0.035	0.02	Yellow = 0.04
	4.60	0.035	0.02	Red = 0.02
	4.70	0.035	0.02	
	4.80	0.035	0.02	
	4.90	0.035	0.02	
	5.00	0.035	0.02	

Table No. 1 will at least serve as a rapid method for the standardizing of the stock bottles of natural waters, as the observer's eye becomes trained and more knowledge is obtained of the conditions which influence readings, a more perfect scale may be constructed.

The direct use of the instrument with the construction of a chart for each water, is evidently out of the question where, as in our laboratory, the color must be determined on twenty or thirty samples a day.

A modification of the tintometer has been proposed by H. R. Proctor, Yorkshire College, Leeds, England.<sup>1</sup>

This is designed to bring the color patches into juxtaposition as is done in the comparison of two spectra instead of having the separating dark band in the centre. We have not been able to try this instrument, but it promises to be an improvement.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 15.]

## ON THE ESTIMATION OF LEVULOSE IN HONEYS AND OTHER SUBSTANCES.

BY H. W. WILBY.

Received September 30, 1895.

A SIMPLE optical method for the estimation of levulose is of great advantage in the examination of honeys and other substances containing that body. The following optical method is one of easy application when the analyst has access to the jacketed observation tube, which will be mentioned below.

The principle of the process rests upon the change in the specific rotatory power of levulose at different temperatures. The change in the optical rotation of other bodies associated with levulose in the conditions of the experiments to be described is so little as to affect the data obtained to a very slight degree. The process, as it has been worked out, is easily applied and gives results which it is believed are better than those obtained by any other method.

*The Observation Tube.*—The most important adjunct of a mechanical nature in the process is an observation tube which

<sup>1</sup> *J. Soc. Chem. Ind.*, 14, 2, 1895.

will permit of the polarimetric reading of a solution containing levulose at widely separated temperatures. The two temperatures adopted for experimental purposes are zero and 88°. The observation tube which was devised for the purpose is so constructed as to permit of its being surrounded entirely by a temperature control medium, either water or ice. Even the cover glasses of the tube devised are subjected to the temperature of the medium. The whole column of liquid under observation can in this way be brought to the same temperature, thus not only securing more accurate results, but removing the difficulties in the way of reading, produced by the refraction of light in passing through liquid media of different densities. The observation tube employed can be made either of glass or metal. The glass tube changes less in length on changing temperatures, but the metal tube is more sensitive and can be brought with its contents more quickly to a definite temperature. A tube, especially constructed for the purpose and made of silver, is particularly convenient in the observation of solutions which have been inverted by the action of hydrochloric acid. When metal tubes are used the continuous kind is employed, permitting the displacement of one solution by another without the removal of the tube from its position. The length of the tube at ordinary temperature having been determined, correction is made for linear expansion or contraction at the temperature of observation. At low temperatures it is impossible to use an observation tube of ordinary construction on account of the deposition of moisture upon the cover glasses. This difficulty is entirely overcome by attaching to the ends of the observation tube, by means of a threaded screw, a tube made of hard rubber carrying a central axis of perforated brass of the same dimensions as the diameter of the observation tube outside of which are placed fragments of calcium chloride. The end of the tube is covered air-tight with an ordinary cover glass. Being screwed air-tight upon the observation tube the calcium chloride at once absorbs all the moisture within the hard rubber cylinder and thus completely protects the cover glass from the deposition of water. Protected in this way the observation tube can be kept for hours at the temperature of zero, without any possibility of obscuring the

field of vision from deposited moisture. The construction of the protecting tube, together with the method of its attachments to the observation tube, is shown in the figure.

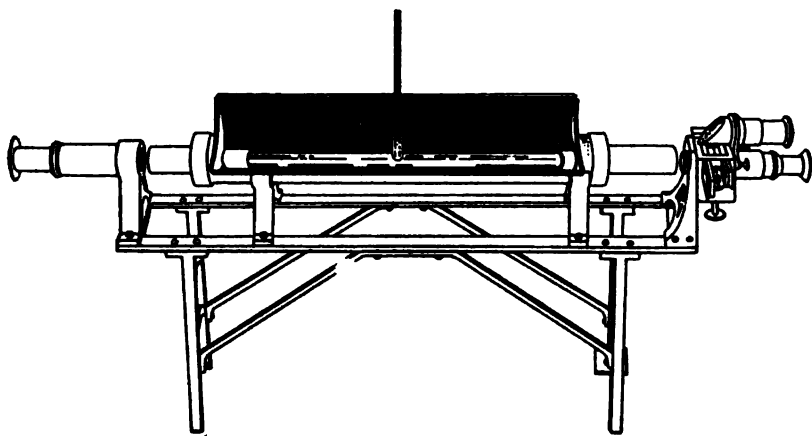


FIG. 1.—APPARATUS FOR POLARIZING LIQUIDS AT LOW TEMPERATURES.

For reading at low temperatures, especially at zero, the observation tube is held in a large metal receptacle coated on the outside with asbestos cloth and having a V-shaped slit above. A special stand is made for holding this apparatus to which is also fixed the optical parts of a double compensating Schmidt & Haensch half shadow polariscope. The construction of the stand and of the holder for the observation tube is shown in the figure, in which, however, the V-shaped slit is pushed down to one side in order that the photograph may show the position of the observation tube within. In practice the V-shaped slit is kept at the top and the observation tube is entirely surrounded by finely ground ice, an opening in the bottom permitting the water to escape as the ice melts.

The details of the construction of the observation tube are shown in a horizontal section through the center of the observation tube in Fig. 2. In this figure the observation tube, made of glass or metal, is represented by *i*, and the metal jacket, open at the top in the V shape as described, by *k*. The observation tube is closed by the heavy disk *b*, made of non-polarizing glass. This disk is pressed against the end of the observation tube by

the rubber washer *a* when the drying system about to be described is screwed on to *k*. The apparatus for keeping the cover glass dry is contained in the hard rubber tube *m*, and consists of a perforated cylinder of brass, *e*, supported at one end by the perforated metal disk *c* and at the outer end by the arm *d*. It is closed by a cover glass of non-polarizing glass *s* and can be screwed on to the system *h* at *n*. The space *p* is filled with coarse fragments of caustic soda, or potash, or calcium chloride by removing the cover glass *s*. The perforated disk *c* prevents any of the fragments from entering the axis of observation.

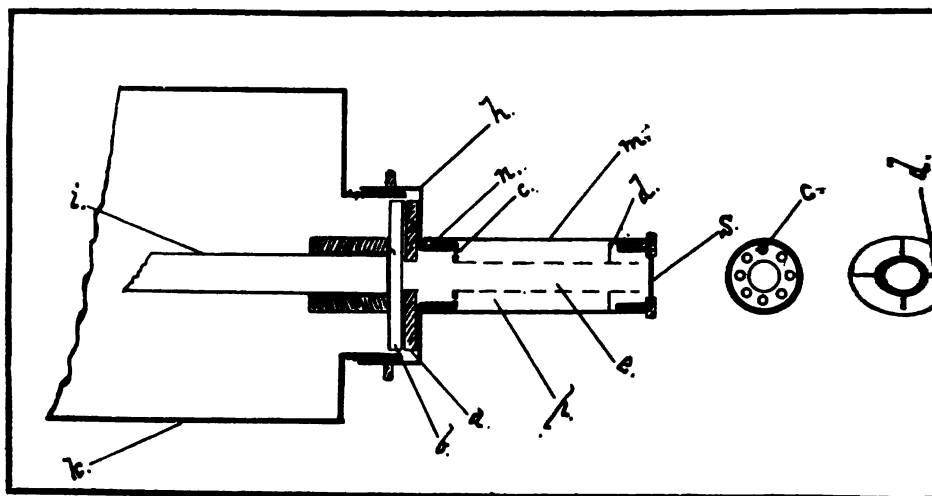


FIG. 2.—DETAILS OF OBSERVATION TUBE.

When the cover glass *s* is replaced, it just touches the free end of the perforated metal tube preventing any of the fragments of the drying material from falling into the center at the outer end. When this drying tube is placed in position, the contents of the observation tube *i* can be kept at the temperature of zero for an indefinite time, without the deposition of a particle of moisture either upon the glass *b* or *s*.

For observation at high temperatures, the apparatus described above may be used or it may be removed from the stand, which is so constructed as to receive a large box covered with as-



bestos felt an inch thick. The observation tube is held within this box in the same way as in the one just described so that the hot water extends not only the entire length of the tube but also covers the cover glasses. In both cases the cover glasses are made of heavier glass and are much larger in diameter than are the ordinary tubes for polariscopes. The protecting cylinders of hard rubber are not needed at high temperatures, but can be left on without detriment.

The illustration, Fig. 3, shows the arrangement of the apparatus with a silver tube, which can be filled and emptied without removing it, in position.

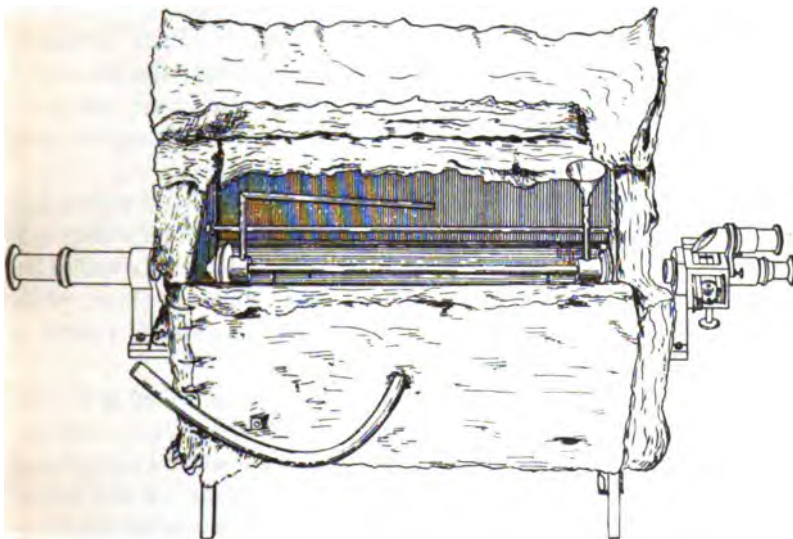


FIG. 3.—POLARISCOPE FOR LEVULOSE AT HIGH TEMPERATURES.

In practice the water is heated with a jet of steam and an even temperature is secured by a mechanical stirrer, kept slowly in motion. With such a box it is easy to keep a temperature for several hours which will not vary more than half a degree. The temperature for reading the hot solutions is fixed at  $88^{\circ}$ , this being the one at which a mixture of equal molecules of levulose and dextrose is optically inactive. In every case the sugar solutions are made up to the standard volume at the

temperatures at which they are to be read, and thus the variations due to expansion or contraction are avoided. When solutions are to be read at a high temperature, they must be made with freshly boiled water so as to avoid the evolution of air bubbles which may otherwise obscure the field of vision.

By means of the apparatus described it is easy for the analyst to make a polarimetric reading at any temperature desired. In all cases the observation tube should be left at least half an hour and sometimes longer, in contact with the temperature control medium before the reading is made. In the case of reading at zero it is also found that it requires several hours for a levulose solution containing other bodies, such as are found in honey, to reach a constant rotatory power. It is therefore necessary, in such cases, to leave the observation tube in contact with finely powdered ice for at least three hours before the reading is made. For ordinary analytical operations, however, this long delay is unnecessary.

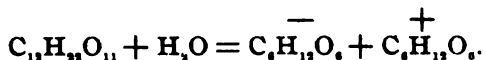
The appearance of the field of vision is usually a pretty fair index of the point of time at which a constant temperature is established throughout all parts of the system. Any variation in temperature produces a distortion of the field of vision, while a constant fixed temperature will disclose the field of vision in its true shape and distinctness of outline.

The chief points of novelty in the apparatus described are, first, the immersion of the whole of the observation tube together with the cover glasses in the temperature medium used; and second, the protection of the external surfaces of the cover glasses from the deposition of moisture at low temperatures.

#### PRINCIPLES OF THE CALCULATION.

If 26.048 grams of pure sucrose be dissolved in water and the volume made up to 100 cc. it will produce an angular rotation of  $34.68^\circ$  when examined in a 200 mm. tube with polarized sodium monochromatic light. Upon the cane sugar scale of an accurately graduated Schmidt and Haensch shadow instrument the reading will be 100 divisions, corresponding to 100 per cent. of pure sucrose.

In the complete inversion of the cane sugar the reaction which takes place is represented by the following formula :



The minus and plus signs indicate that the resulting invert sugar is a mixture of equal parts of levulose (*l* fructose) and dextrose (*d* glucose). We are not concerned here with the fact that a complete inversion of cane sugar is a matter of great difficulty nor with the danger which is always experienced of destroying a part of one of the products of inversion. They are matters which may cause a variation in the analytical data afterward, but do not affect the principles on which the process is based.

In the inversion of 26.048 grams of cane sugar there are therefore produced 13.71 grams of levulose and 13.71 grams of dextrose, or in all 27.42 grams of the mixed sugars.

The angular rotation which would be produced with sodium light, by 13.71 grams of dextrose in a volume of 100 cc. and through a column 200 mm. in length is,  $14.53^\circ$ , equivalent to 41.89 divisions of the cane sugar scale. The specific rotatory power of dextrose solution of the density given is almost exactly 53, and this number is used in the calculations.

In a mixture of the two sugars under the conditions mentioned and at a temperature of  $0^\circ$ , the angular rotation observed is  $-15.15^\circ$  equivalent to 43.37 divisions of the cane sugar scale.

The  $+$  rotation due to the dextrose present is  $14.53^\circ$ . Therefore, the total negative rotation due to levulose at  $0^\circ$  is  $15.15 + 14.53 = 29.68^\circ$ . The specific rotatory power, therefore, of levulose at  $0^\circ$  and in the degree of concentration noted is readily calculated from the formula

$$-(\alpha)_D^0 = -\frac{29.68 \times 100}{2 \times 13.71} = 108.24.$$

Since at  $88^\circ$  the mixture of levulose and dextrose is neutral to polarized light, it follows that at that temperature the specific rotatory power of levulose is equal to that of dextrose, *viz.*  $53^\circ$ .

$$-(\alpha)_D^{88^\circ} = -53^\circ.$$

The total variation in the specific rotatory power of levulose, between zero and  $88^{\circ}$ , is  $108.24 - 53 = 55.24^{\circ}$ . The variation for each degree of temperature, therefore, of the specific rotatory power of levulose is equal to  $55.24$  divided by  $88$ , which is equal to  $0.628^{\circ}$ . From these data it is easy to calculate the specific rotatory power of levulose for any given temperature. For instance, let it be required to determine the specific rotatory power of levulose at a temperature of  $20^{\circ}$ . It will be found equal to  $108.24 - 0.628 \times 20 = 95.68^{\circ}$ .

In these calculations the influence of the presence of hydrochloric acid upon the rotatory power of the levulose is neglected.

Since the variation in angular rotation in the mixture at different temperatures is due almost wholly to the change in this property of the levulose, it follows that the variation for each degree of temperature and each per cent. of levulose can be calculated. Careful experiments have shown that the variation in the rotatory power of levulose between  $0^{\circ}$  and  $88^{\circ}$  is represented by a straight line. For  $13.71$  grams per  $100$  cc. the variation for each degree of temperature is equal to  $43.37 \div 88 = 0.49$  division on the cane sugar scale or  $15.15 \div 88 = 0.1722^{\circ}$  angular measure. If  $13.71$  grams of levulose in  $100$  cc. produce the deviations mentioned for each degree of temperature, one gram would give the deviation obtained by the following calculations:

For the cane sugar scale,

$$0.49 \div 13.71 = 0.0357^{\circ}$$

And for angular rotation,

$$0.1722 \div 13.71 = 0.01256^{\circ}.$$

The above data afford a simple formula for calculating the percentage of levulose present from the variation observed in polarizing a solution containing levulose, provided that the quantity of levulose present is approximately fourteen grams per  $100$  cc.

Suppose in a given case the difference of reading between a solution containing an unknown quantity of levulose at  $0^{\circ}$  and  $88^{\circ}$  is equal to thirty divisions of the cane sugar scale. What weight of levulose is present? We have already seen that one gram in  $100$  cc. produces a variation of  $0.0357$  division for  $1^{\circ}$ . For  $88^{\circ}$  this would amount to  $3.1416$  divisions. The total

weight of levulose present is therefore  $30 \div 3.1416 = 9.549$  grams. In the case given 26.048 grams of honey were taken for the examination. The percentage of levulose was therefore  $9.549 \div 26.048 = 36.66$  per cent.

If it be inconvenient to determine the polarimetric observations at temperatures so widely separated, as  $0^{\circ}$  and  $88^{\circ}$  the interval may be made less. In the above case if the readings had been made at  $20^{\circ}$  and  $70^{\circ}$  the total variation would have been only 50/88 of the one given, *viz.*: 17.05 divisions of the cane sugar scale. The calculation would then have proceeded as follows :

$$0.0357 \times 50 = 1.785.$$

Then  $17.05 \div 1.785 = 9.552$  grams of levulose, from which the actual percentage of levulose can be calculated as above.

For honeys the operation is to be conducted as follows:

Since honeys contain approximately twenty per cent. of water and in the dry substance have approximately forty-five per cent. of levulose, about 38.50 grams of the honey should be taken to get approximately 13.8 gram of levulose.

In the actual determination the calculations may be based on the factors above noted, but without respect to the degree of concentration. If only half the quantity of dextrose noted be present its specific rotatory power is only reduced to  $52.75^{\circ}$  and this will make but little difference in the results. In the case of honey only 13.024 grams of the sample are used in the examination, half the normal weight for the Ventzke sugar scale. The error however due to difference in concentration is quite compensated for by the ease of clarification and manipulation. Alumina cream alone is used in the clarification, thus avoiding the danger of disturbing the rotatory power of the solution due to the presence of an excess of lead acetate.

An interesting fact is observed in cooling solutions of honey to  $0^{\circ}$ . The maximum left-handed rotation is not reached as soon as the temperature reaches  $0^{\circ}$ , but only after it has been kept at that temperature for two or three hours. The line representing the changes in rotatory power, in solutions of honey between  $0^{\circ}$  and  $88^{\circ}$ , is practically straight but from  $10^{\circ}$  to  $0^{\circ}$ , if measured by the readings taken without delay, it is decidedly

curved; the reading being less at first than it really is afterwards. After three hours the  $0^\circ$  becomes sensibly constant and then the whole line is nearly straight but still with a slight deficiency in the reading at the  $0^\circ$ . For this reason the computations should be based on readings between  $0^\circ$  and  $88^\circ$  rather than on a number covering the whole range of temperature. Nevertheless, if the solution be kept at  $0^\circ$  for three hours before the final reading is taken no error of any practical magnitude can be introduced.

The calculations given above for the cane sugar scale can also be made in an exactly similar manner for angular rotation. The angular variation produced by one gram of levulose for  $1^\circ$  of temperature is  $0.01256^\circ$ . For  $88^\circ$  this would become  $1.10528^\circ$ . Suppose the total observed angular deviation in a given case between  $0^\circ$  and  $88^\circ$  to be  $10.404^\circ$ . Then the weight of levulose present is  $104.04 \div 1.10529 = 9.413$  grams.

In the case mentioned 26.048 grams of honey were taken for the examination. The percentage of levulose present therefore was  $9.413 \div 26.048 = 36.13$ .

#### GENERAL FORMULA FOR THE CALCULATION OF PERCENTAGE OF LEVULOSE.

Let  $K$  = deviation in divisions of cane sugar scale or in angular rotation produced by one gram of levulose for  $1^\circ$  temperature.

Let  $T$  and  $t$  = temperatures at which observations are made.

Let  $R$  = observed deviation in rotation.

Let  $W$  = weight of levulose obtained.

Let  $L$  = per cent. of levulose required.

Then 
$$L = \frac{R}{K(T-t)} \div W.$$

In most genuine honeys the value of  $R$  between  $0^\circ$  and  $88^\circ$  is approximately thirty divisions of the cane sugar scale or  $10^\circ$  angular measure for 26.048 grams in 100 cc. read in a 200 mm. tube, or for 13.024 grams in 100 cc. read in a 400 mm. tube.

The method of analysis outlined above has been applied in the examination of a large number of honeys with most satisfactory results. It can also be applied with equal facility to other substances containing levulose.

## NOTES ON A FEW PYRIDINE ALKYL IODIDES.<sup>1</sup>

BY ALBERT B. PRESCOTT.

Received November 27, 1895.

### PYRIDINE METHYL IODIDE.<sup>2</sup>

**Preparation.**—Of rectified pyridine, boiling at 116°–118° C., fifteen cc. are taken in a flask immersed in cold water and carrying a reflux condenser, and twelve cc. methyl iodide added, in very small portions at first, when the reaction is violent. Boiling is moderated by the rate of the addition. After standing half an hour, the resulting crystalline mass, light straw colored, is warmed on the water-bath without the condenser, and more methyl iodide very gradually added until, as a result, the odor of pyridine disappears. Any excess of methyl iodide is distilled off on the water-bath. The mass is now dissolved in sufficient warm absolute alcohol, from which it crystallizes on cooling, and the product recrystallized in the same way several times, until colorless crystals are obtained. Colorless crystals are sometimes obtained in the second crystallization. From alcohol of ninety to ninety-five per cent. strength the crystallization is much less satisfactory. The mother liquids, on the addition of ether, yield a considerable precipitate of the product, and this can be crystallized from absolute alcohol.

**Properties.**—The crystals are flat pencils, sometimes aggregated in rosettes. They are very soluble in water, soluble in alcohol, methyl alcohol, chloroform, acetone, and in glacial acetic acid; not soluble in ether, or benzene, or carbon disulfide. The crystals are very slowly deliquescent, to a degree scarcely affecting weight after several hours exposure to the air. The melting point is 117° C.

<sup>1</sup> Read at the Springfield meeting of the American Association for the Advancement of Science, Aug. 30, 1895.

<sup>2</sup> From the experimental work of Mr. P. F. Trowbridge. Anderson stated the additive reaction of pyridine with alkyl iodides in 1835. In making such an addition-product, as a means of distinguishing pyridine from its homologues in analysis, he took ethyl iodide, *Ann. Chem.* (Liebig), 94, 364. Hofmann resorted to pyridine in his study of the reaction of dihalogen substituted hydrocarbons with tertiary bases, but not earlier, that I have been able to find.—1861: *Proc. Roy. Soc.*, 11, 261. O. Lange, in 1885, in the course of work on the formation of picolines by Ladenburg's method of transposition, gives some account of pyridine methiodide.—*Ber. d. chem. Ges.*, 18, 3436. O. de Coninck, in 1883, proposed the additive reactions with methyl iodide in contrast with those of ethyl iodide for distinction between pyridine derivatives and quinoline derivatives.—*Bull. Soc. Chim.* [2], 40, 276.

PYRIDINE ETHYL IODIDE.<sup>1</sup>

*Preparation.*—It has been directed to bring about the addition of ethyl iodide to pyridine by heating the mixture of the two in sealed tubes. Trial was made of three ways, (1) by heating in sealed tubes at 120° C.; (2) by heating in pressure flasks at 100° C.; (3) by occasionally shaking in a flask at the temperature of the room. The last stated method gives much the best results. The ethyl iodide should be taken in a slight excess of the chemical proportion, and added all at once. With considerable quantities the heat of chemical action after a short time needs to be moderated by cooling, to prevent vaporization of the materials. The action is usually complete within two hours, the contents of the flask becoming solid. The crystalline mass is dissolved in enough warm absolute alcohol, and crystallized, more perfectly by the low temperature of a freezing mixture, recrystallizing until white. Addition of ether to the absolute alcoholic solution causes crystalline precipitation, and in this way the mother liquids may be made to yield final portions. Like addition of chloroform precipitates an oily mass.

*Properties.*—The crystals are colorless plates, permanent or slightly deliquescent, soluble in water, alcohol, methyl alcohol, acetone, and glacial acetic acid, from which it crystallizes, and slightly soluble in ethyl acetate; insoluble in ether, benzene, carbon disulphide, and in chloroform. The melting point is 90.5° C.

PYRIDINE PROPYL IODIDE,<sup>2</sup>  $C_5H_5N.CH_2CH_2CH_2I$ .

*Preparation.*—Pyridine rectified to boil at 116.5°–118.5°, and normal propyl iodide distilling at 102° C., are taken in molecular proportions of the two, but with a slight excess of the iodide. The two are digested together under pressure in a sealed tube at 130° C., for an hour. On cooling the resulting yellowish mass is dissolved in warm absolute alcohol, from which plate-form crystals of the addition product separate on cooling. If

<sup>1</sup> From the experimental work of P. F. Trowbridge in this laboratory. T. Anderson, 1855; *Trans. Roy. Soc. Edinb.*, 21, (4) 571; *Ann. Chem.* (Liebig), 94, 364. O. de Coninck, 1883; *Bull. Soc. Chim.* [2], 40, 276.

<sup>2</sup> From the experimental studies of Mr. S. H. Baer. In Ladenburg's account of the formation of propylpyridine hydriodide, by transposition of pyridine propyliodide (*Ber. d. chem. Ges.*, 17, 772) no description of the last named body is given.



not white it is to be recrystallized from the same solvent. Addition of ether to the absolute alcohol solution throws it down in a crystalline precipitate. Like addition of chloroform separates it as an oil-like liquid. From alcohol of ninety-five per cent. it is precipitated as an oil by addition of ether. In analysis of the preparation, it gave for iodine 50.63 per cent. in comparison with 51.00 per cent. by calculation.

*Properties.*—In colorless plate-form crystals, deliquescent, soluble in water, alcohol, amyl alcohol, ethyl acetate, and in benzene; insoluble in ether and in chloroform. The melting-point is between 52° and 53° C.

PYRIDINE ISOPROPYL IODIDE,<sup>1</sup>  $C_5H_5N.(CH_3)_3CHI$ .

*Preparation.*—By the same method, and under the same conditions already given for the corresponding normal propyl compound, but using a greater excess of the alkyl iodide, namely about one and a half molecules of the isopropyl iodide (boiling at 89°–90° C.) to one molecule of pyridine. The product solidifies in a crystalline mass while in the sealed tube, more readily and completely than the product of normal propyl iodide and pyridine, and it crystallizes more readily from absolute alcohol. In analysis, the iodine found was 50.64 and 50.50 per cent. in comparison with 51.00 per cent. by calculation.

*Properties.*—Colorless crystals, soluble in water, alcohol of ninety-five per cent., and in ethyl acetate; less freely soluble in absolute alcohol, amyl alcohol, or chloroform; insoluble in ether. The melting point is 114°–115° C.

#### COMPARISON OF MELTING POINTS.

As set forth below the addition compounds of the one base pyridine with different alkyl iodides,  $C_nH_{m+1}I$  show a gradation of melting points, a gradation which appears among the homologous normal members of the series, and again appears between isomeric members. The solubilities of these addition compounds show a correspondence to their melting points, agreeing with the generalization of Carnelly.<sup>2</sup> Pyridine

<sup>1</sup> From the work of Mr. S. H. Baer in this laboratory. Schrader (Inaug. Diss. at Kiel, 1884) obtained this quaternary iodide, by treatment at 100° C., as a yellow-white crystalline mass, convertible to the corresponding chloride (Ladenburg's *Handwörterbuch*, 9, 464. Ladenburg and Schrader, *Ber. d. chem. Ges.*, 17, 1121).

<sup>2</sup> *Phil. Mag.*, (5) 13, 190; *J. Chem. Soc.*, 53, 782.

combination has been resorted to for various characteristics distinctive of alcohol radicals, by de Coninck, as cited in the beginning of this paper, and by Lippert<sup>1</sup> in 1893. The iodides of these quaternary bases give constants more distinctive of composition than do the platinum chlorides, at least so far as melting points of the iodides are available. In tabulating the melting points of the pyridine alkyl iodides it appears that, comparing homologues and again comparing isomers, the melting points of the addition products *fall* as the boiling points of the free alkyl iodides *rise*.<sup>2</sup> The same reverse ratio appears among picoline alkyl iodides. On the contrary, comparing pyridine methyl iodide with picoline methyl iodide, the two tertiary bases being homologous and the alkyl iodide being the constant factor, it is found that the melting point of the addition compound rises as the boiling point of the tertiary base rises, and in an extreme proportion.

#### QUATERNARY BASE IODIDES.

##### *With homologous alkyls:*

	Melting points	Boiling points of the free alkyl iodides.
Pyridine methyl iodide.....	117° <sup>3</sup>	45°
Pyridine ethyl iodide.....	90.5° <sup>3</sup>	72°
Pyridine propyl iodide.....	52-53° <sup>4</sup>	102°
(Pyridine butyl iodide decomposes before melting <sup>5</sup> .....		130°)
<i>a</i> -Picoline methyl iodide.....	226.5-227° <sup>6</sup>	45°
<i>a</i> -Picoline ethyl iodide;.....	under..... 100° <sup>7</sup>	72°

##### *With isomeric alkyls:*

Pyridine isopropyl iodide.....	114-115° <sup>4</sup>	89°
Pyridine propyl iodide.....	52-53° <sup>4</sup>	102°

#### QUATERNARY BASE METALLIC CHLORIDES.

(Pyridine tertiary butyl salts are not formed) <sup>8</sup> .....		100°
Pyridine isobutyl platinum chloride.....	220° <sup>6</sup>	119°
" " gold chloride.....		139° <sup>8</sup>

<sup>1</sup> *Ann. Chem. (Liebig)*, 276, 182.

<sup>2</sup> This reverse ratio does not hold good between ethyl and isopropyl, in their pyridine iodo-products, the one being not the direct homologue, but the isomer of the homologue of the other. In 1882 Carnelly remarked of "isomeric compounds" as shown by many instances, that their melting points follow a rule the reverse of that accepted for their boiling points, namely that "those melt the highest in which there are the greatest number of side chains." (*Phil. Mag.* (5), 13, 126).

<sup>3</sup> Trowbridge.

<sup>4</sup> Baer.

<sup>5</sup> Lippert: *Ann. Chem. (Liebig)*, 276, 182.

<sup>6</sup> Ramsay: *Phil. Mag.* (5), 4, 241. Before the constitution of picoline was established. It is not necessary here to distinguish between isomeric picolines.

<sup>7</sup> Anderson: *Ann. Chem. (Liebig)*, 94, 361.

	Melting points.	Boiling points of the free alkyl iodides.
Pyridine secondary butyl platinum chloride	191° <sup>1</sup>	119°
"    "    gold chloride.....	129° <sup>1</sup>	
Pyridine normal butyl platinum chloride ..	205° <sup>1</sup>	130°
"    "    "    gold chloride .....	111° <sup>1</sup>	
<i>With homologous tertiary bases :</i>		The free tertiary bases.
Pyridine methyl iodide.....	117° <sup>2</sup>	116°
Picoline methyl iodide .....	226.5-227° <sup>2</sup>	132-140°
<i>Comparing two isomeric addition compounds :</i>		Ter. base. Alk. iod.
Pyridine ethyl iodide, C <sub>5</sub> H <sub>5</sub> N.C <sub>2</sub> H <sub>5</sub> I =		
C <sub>7</sub> H <sub>10</sub> NI .....	90.5° <sup>2</sup>	116° 72°
Picoline methyl iodide, CH <sub>3</sub> .C <sub>5</sub> H <sub>4</sub> N.CH <sub>3</sub> I =		
C <sub>7</sub> H <sub>10</sub> NI.....	227° <sup>2</sup>	132° 45°

In the comparison last above, there are two quaternary base iodides having the same empirical formula, and having near the same mean of boiling points of the uniting constituents, while the difference between their quoted melting points is something surprising. We should expect, however, from analogy with the previous comparisons, to find a double homologous difference in this case. The transfer of the homologous CH<sub>3</sub>, so to speak, from the alkyl of one compound to the amine of the other compound, should exert a two-fold effect in raising the melting point.

In a paper by Mr. Flintermann<sup>4</sup> and myself, some data are given in small part from our own work and more from the work of others, as to the limits of additive combination of isomeric alkyls with tertiary amines, especially with pyridine, in formation of quaternary bases. It would seem desirable to compare these apparent limits of additive formation with the generalizations of Carnelly and others upon the cohesion constants of isomers at large. Therewith these few facts of the melting points of pyridine quaternary bases are presented, though requir-

<sup>1</sup> Lippert: *Ann. Chem.* (Liebig), 276, 182.

<sup>2</sup> Trowbridge.

<sup>3</sup> Ramsay: *Phil. Mag.* (5), 4, 241. Before the constitution of picoline was established. It is not necessary here to distinguish between isomeric picolines.

<sup>4</sup> Dipyrindene trimethylene dibromide, etc., this Journal, 18, 28.

ing more data, with the re-examination of figures of early date, as a part of the study of the chemical character of the nitrogen bases. To the same end some work upon the hydroxides of these bases is nearly ready for presentation from this laboratory. And to the same end work is being continued upon the periodides,<sup>1</sup> and other super halides, that these extreme additive combinations may show something of the base making power of nitrogen.

UNIVERSITY OF MICHIGAN.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

### AN ELECTROLYTIC METHOD FOR THE DETERMINATION OF MERCURY IN CINNABAR.

BY W. B. RISING AND VICTOR LENNER.

Received November 12, 1899.

WHEN a rapid solution of cinnabar is desired, heretofore, oxidation with aqua regia has seemed most convenient; the length of time required to expel the nitric acid used, and the likelihood of loss of mercury by distillation in hydrochloric acid, are serious hindrances to the use of this method. Hydrobromic acid dissolves very readily mercuric sulphide, as well as many other naturally occurring sulphides with the evolution of hydrogen sulphide and the formation of the bromide.

If this solution be nearly neutralized with caustic potash, pure potassium cyanide added in sufficient excess to dissolve the cyanide first precipitated (Smith, *Electro-Chemical Analysis*, p. 58), and electrolyzed with a weak current, the mercury will be readily deposited as metal on a platinum dish used as a negative electrode. The use of hydrobromic acid is to be recommended, as it gives such a ready method of decomposition, and can be used at low temperatures, when there will be no loss of mercury by distillation.

The hydrobromic acid used in the following experiments was prepared by treating potassium bromide with sulphuric acid of 56° Baumé; the gas was conducted into water, as in the preparation of hydrochloric acid. By using potassium bromide

<sup>1</sup> This Journal, 17, 775, 899.

with the above strength of acid, hydrobromic acid quite free from bromine, can be readily prepared.

The ordinary hydrobromic acid used in the laboratory, containing bromine, could be used in the following experiments :

The first sample which was worked with was pure mercuric sulphide. Hydrobromic acid of constant boiling point, *i. e.*, forty-nine per cent. was diluted with water one to four, and the sample treated with as little excess as possible over what would be necessary for its solution ; the slight excess of acid was neutralized with potassium hydroxide, potassium cyanide added in excess and the solution electrolyzed by a current giving 0.025 amperes N. D.<sub>100</sub>.

The following results were obtained :

Mercuric sulphide. gram.	Mercury found. gram.	Mercury. Per cent.
0.2110	0.1818	86.16
0.2058	0.1774	86.20

The second sample was a naturally occurring cinnabar ; determination (*a*) was made, using the decomposition by aqua regia, evaporating off the excess of nitric acid with hydrochloric, neutralizing the excess of hydrochloric acid with potassium hydroxide, adding potassium cyanide in excess and electrolyzing as before. (*b*) and (*c*) were treated with twenty per cent. hydrobromic acid at the boiling temperature ; solution was effected in a few minutes, the excess of acid was neutralized by potassium hydroxide, potassium cyanide added in excess and electrolyzed with the same strength of current as before.

Results were :

	Cinnabar. gram.	Mercury found. gram.	Mercury. per cent.
( <i>a</i> ).....	0.2024	0.1046	51.68
( <i>b</i> ).....	0.2514	0.1299	51.67
( <i>c</i> ).....	0.5135	0.2656	51.72

The last sample was a lower grade cinnabar, very silicious, and long digestion with either hydrobromic acid or aqua regia was necessary. In this last experiment the action of the hydrobromic acid was very much more rapid than that with aqua regia. The mercury was deposited from a cyanide solution as before.

Results were, using hydrobromic acid as solvent :

	Cinnabar. gram.	Mercury found. gram.
(a).....	0.2011	0.0616
(b).....	0.2011	0.0622

Using aqua regia as solvent :

	gram.	gram.
(a).....	0.2030	0.0629
(b).....	0.2030	0.0631

### NEW BOOKS.

THE SCIENTIFIC FOUNDATIONS OF ANALYTICAL CHEMISTRY TREATED IN AN ELEMENTARY MANNER. BY WILHELM OSTWALD. TRANSLATED BY GEORGE M'GOWAN. xviii, 207 pp. 8vo. London and New York : Macmillan & Co. Price, \$1.60.

The little book before us undertakes, as its title indicates, a scientific presentation of the principles which underlie the physico-chemical phenomena upon which the art of analyses depends for the separation, detection and determination of the various substances with which it deals. In this undertaking the electrolytic dissociation theory is freely made use of and with such success that a flood of light is let in upon many of the obscurer phenomena encountered in the ordinary course of analysis.

The presentation of the subject is elementary in the best sense, but little in the way of previous knowledge being assumed, while by the clearness of statement and logical order of ideas preserved throughout, the author has fairly deserved the right to be named with the great masters of scientific style, with Tyndall and with Hofmann.

The theory and its applications are separately considered. Under the former head we find a discussion of the theory of the washing of precipitates and of the adsorption phenomena which are of such importance in that process, further, of physical methods of separation, such as distillation, of the law of mass action, of supersaturation and of many other topics, the treatment of all being condensed and full of suggestions to the thoughtful reader.

In the special or applied part the analytical reactions of the metallic and acidic ions of the various analytical groups are taken up in detail, but briefly.

Lest it should be thought that this work is a piece of special pleading in behalf of the electrolytic dissociation theory, it is but just to the author to state that though written from the stand-point of that theory, the book is not *doctrinaire*, but is broad enough to be read with much interest by all chemists, whether they agree with the author's special views or not.

Much credit is due to Dr. M'Gowan for the smooth and scholarly translation now placed at the disposal of the English reading public, which annihilates the only excuse any English speaking chemist could offer for unfamiliarity with the most important work on the theory of analysis which has ever appeared.

LAUNCELOT ANDREWS.

PRACTICAL PROOFS OF CHEMICAL LAWS. BY VAUGHAN CORNISH.  
New York: Longmans, Green & Co. Price 75 Cents.

This little work adopts a practical method for the explanation of "Dalton's Atomic Theory and the Laws of Combining Proportions." The first chapter is devoted to statements of these laws, and is followed by a chapter on the use of the balance. These prepare the student for the subsequent six chapters; which are devoted to the experimental part, in each case preceded by a list of the necessary apparatus and followed by an example and an account of the original experiments, together with references to the original literature. The experiments are well chosen, calculated to give good results with simple and inexpensive reagents and apparatus. The arrangement is a time-saving one, and where time for laboratory work is very limited, as in higher schools, this fact will figure largely.

HERMANN FLECK.

ORGANIC CHEMISTRY. THE FATTY COMPOUNDS. BY R. LLOYD WHITELEY, F.I.C., F.C.S. New York: Longmans, Green & Co. 1895. 8vo. viii, 291 pp. Price, \$1.00.

The publication of this manual, strikingly similar in purpose, arrangement and matter to the "Organic Chemistry, Part I," of Perkin and Kipping, issued last year, shows that the needs of elementary students of this department of chemistry are now recognized more generally than they have been heretofore, and indicates, perhaps, that the number of chemists, who feel able to

supply their needs, is increasing. Whether this latest effort to make a satisfactory text-book is successful, can be determined only by giving the book a trial. Without unnecessary detail, the author has furnished a clear presentation of the main facts and theories pertaining to the "fatty compounds," giving also directions for the preparation in the laboratory of many compounds, and methods for their identification. These directions are generally clear and accurate.

The discussion of stereochemical theories is hardly full enough even for an elementary book, and the average student would probably find the chapters on the polyhydric alcohols and their derivatives more intelligible and interesting, if some of the methods recently employed for their synthesis and study, had been briefly explained. The book is attractively printed, and has a satisfactory index.

L. B. HALL.

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### BOOKS RECEIVED.

**How to Disinfect:** A guide to practical disinfection in every-day life, and during cases of infectious illness. By C. T. Kingzett, F. I. C., F. C. S. New York: The American and Continental "Sanitas" Co., Ltd. Price ten cents.

**Elements of Modern Chemistry.** By Charles Adolphe Wurtz. Fifth American edition. Revised and enlarged by Wm. H. Greene, M. D., and Harry F. Keller, Ph. D. Philadelphia: J. B. Lippincott Co. 808 pp. Price \$1.80.

**Nineteenth Annual Report of the Connecticut Agricultural Experiment Station.** Part II. Fertilizers. New Haven: Tuttle, Morehouse and Taylor Press. 74 pp. 1895.

**Bulletin No. 58.** Cutworms in Kentucky. Kentucky Agricultural Experiment Station. Lexington, Ky. 1895. 21 pp.

**Bulletin No. 118.** Cottonseed Hulls and Meal for Beef Production. North Carolina Experiment Station. Raleigh, N. C., July 1895. 37 pp.

**Bulletin No. 119.** Volumetric Estimation of Phosphoric Acid. North Carolina Agricultural Experiment Station. Raleigh, N. C., August, 1895. 24 pp.



# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 11.]

### ACTION OF ACID AMIDES UPON BENZOIN.<sup>1</sup>

BY ALFRED NEWLIN SKAL.

Received November 29, 1895.

THE reactions of benzoïn with a great number of bodies have been very extensively studied, but except the work of Anschütz and Gelderman<sup>2</sup> with urea and thiourea, no work has been done with the extensive class of acid amides. It was with the view of studying how these bodies would react with benzoïn that this work was undertaken. It seemed very probable that by heating the amides with benzoïn a condensation would be effected, as the hydrogen and the amido group of the former, as well as both the carbonyl and hydroxyl group of the latter, are very reactive. It was hoped in this way to prepare a series of condensation products from the amides of the homologous acids of the fatty and of the aromatic series. With this object in view, benzoïn was heated in sealed tubes with various acid amides, in the presence of alcohol as a solvent, in varying proportions and under different conditions of time and of temperature.

Instead of finding the expected series of condensation products, however, it was discovered that with all the simple amides of both the mono- and dibasic acids of the fatty series, and with

<sup>1</sup> From the author's thesis presented to the University of Pennsylvania for the Degree of Ph.D., 1895.

<sup>2</sup> *Ann. Chem. (Liebig)*, 261, 129.

two examples of the amides of the aromatic series, the reaction was preceded by the breaking down of the amide and the subsequent action of the ammonia on the benzoin, giving as the chief product of the reaction tetraphenylazine  $C_6N_2(C_6H_5)_4$ . The constitution of this body has been very carefully worked out by Japp and Wilson<sup>1</sup> and Japp and Burton.<sup>2</sup>

Not until after the action of several of the series had been tried with benzoin was the above conclusion reached, hence the following is a record of the reactions tried and of the results obtained. The work was carried out to a great extent in sealed tubes, the yields obtained were in many cases very small, the separation of the bodies produced difficult, and in some cases impossible, while the analyses were frequently extremely troublesome, as tetraphenylazine is remarkably stable and, as the experience of others has also shown, very difficult to analyze. As an instance of this, in one analysis, after six hours heating to redness with oxide of copper in a current of oxygen, graphitic carbon was found still remaining in the bottom of the boat. Later chromate of lead was used and the difficulties in great measure overcome.

#### I. GENERAL METHOD PURSUED IN STUDYING THE REACTIONS.

As the reactions of benzoin, with ten different amides, were studied, and the identification of the products proved more difficult than was anticipated, no attempt was made to induce condensation by means of dehydrating agents. In all the experiments, unless otherwise stated, benzoin and the amide, in definite, but varying proportions, were heated together with alcohol in sealed tubes. The amount of alcohol used at first was considerable, but the loss from explosions was so great that eventually the tubes were filled to but one-fifth or sixth of their capacity. When the tubes were opened there was generally a very considerable pressure. The presence of ammonia was very evident, and in many cases an ethereal odor was easily detected. Even if no ammoniacal odor could be detected, the alkaline reaction of the tube contents was always decided. Analyses of the gases obtained from the tubes showed from twenty-five per cent.

<sup>1</sup> *J. Chem. Soc.*, 49, 825.

<sup>2</sup> *Ibid.*, 49, 843, and 51, 98.

to thirty-three per cent. of free ammonia. As the chief product of the reaction was identified as tetraphenylazine, and the accompanying bodies were those also produced by the action of ammonia on benzoïn, there can be no doubt as to the interpretation of the result. Under the influence of the heat and alcohol the amide breaks down with the liberation of ammonia, and the formation of an ester with the alcohol. The ammonia then reacts with the benzoïn, as has been already studied by Japp, Wilson and Burton.<sup>1</sup>

Japp and Wilson, in their study of the action of ammonia on benzoïn, have reviewed the ground previously studied by Laurent<sup>2</sup> and by Erdmann<sup>3</sup> and found the products of the reactions to be tetraphenylazine  $C_6N_4(C_6H_5)_4$ , benzoïniam  $C_{10}H_{11}N_2O$ , benzoïnindam  $C_{10}H_{11}NO$ , and lophine  $C_6N_2H(C_6H_5)_2$ . In the study of the products of reaction with the amides, the presence of tetraphenylazine was proved in all cases, the presence of lophine in but one, benzamide, while another body was obtained which proved to be a mixture of the benzoïniam and benzoïnindam of Japp and Wilson.

The tetraphenylazine was identified by analysis, melting point, crystalline form, solubilities, color reaction with sulphuric acid, and also by a determination of the molecular weight. In the work, as given in detail later, some or all of these means of identification were used in each case. Lophine was identified by its melting point. It was only obtained with benzamide as the reacting body, and then only in very small amount. The apparent reason for its occurrence in this case will be discussed under the work with benzamide.

The other body obtained had, under various conditions, different melting points, and did not give concordant results when the different preparations were analyzed. Various methods of fractional crystallization and sublimation were tried to separate it into bodies of definite composition, but without success. With the exception of its solubility in alcohol, all its reactions indicated, as already stated, a mixture of benzoïniam and benzoïnindam.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Jab. phys. Wiss.*, 18, 354, and 26, 266.

<sup>3</sup> *Ann. Chem.* (Liebig), 135, 181.

This action of the acid amides with benzoin, as essentially that of ammonia alone, is entirely in accord with the results obtained by Mason.<sup>1</sup> He found that oxamide and acetic acid heated together in sealed tubes at 220°–230°, reacted with the formation of acetamide.

## II. ACTION OF THE AMIDES OF THE FATTY SERIES UPON BENZOIN.

*a. Malonamide and Benzoin.*—Malonamide and benzoin, in molecular proportions, were heated with alcohol on the water-bath in a flask connected with a return condenser for an hour. An examination of the material showed that no change had taken place, only benzoin and malonamide being found. The two bodies, in the same proportion, were then heated with alcohol in a sealed tube to 110° in a paraffine bath. As no change took place the tube was then heated at temperatures varying from 130° to 190°, with but little apparent change. The tube was then heated for eighteen hours at 200°. When opened a considerable pressure was evident and the odor of ammonia was very decided. The contents of the tube were poured out, and the crystals which had separated were filtered from the deep yellow liquid, pressed between filter-paper and treated several times with warm chloroform. Everything dissolved except a small amount of unchanged malonamide. The filtered solution was then evaporated nearly to dryness, the residue warmed with alcohol to remove coloring-matter, boiled four times with alcohol, and the insoluble portion dissolved in chloroform. From the first alcoholic filtrate on cooling crystals were obtained, melting, not at all sharply, at 190°–217°. The second filtrate gave white needles, melting at 192°–206°; the third filtrate crystals of the same form in less amount, melting at 193°–206°. The other two alcoholic filtrates yielded thicker needles in small quantity, melting at 243°–244°.

The three portions of crystals with the lower melting point were united and alternately treated with warm and boiling alcohol. By this means a series of products was obtained with all degrees of melting points between 193° and 220. As the mate-

<sup>1</sup>*J. Chem. Soc.*, 55, 107.

rial is all easily soluble in chloroform and in benzoïn, this gave no means of separation. An attempt at separation by means of sublimation was equally unsuccessful, the products showing the same wide range of melting point.

The three lots of crystals with high melting point and evidently much less soluble in alcohol than the other body, were united, warmed with alcohol, and the residue dissolved in chloroform. On concentration of the solution large transparent crystals were obtained with a melting point of  $245^{\circ}$ .

The above method of separation and purification has been given in detail, as it was used with all the amides. Many portions of benzoïn and malonamide were subjected to the above treatment, and the product with the melting point of  $245^{\circ}$  was proved to be tetraphenylazine by the results of the following examination :

	Substance.	H <sub>2</sub> O	CO <sub>2</sub>
I.	0.1351	0.0611	0.4384
II.	0.1416	0.0637	0.4585
III.	0.1339	0.0568	0.4343
IV.	0.2004 gram burned with copper oxide gave 13.8 cc. nitrogen at $26^{\circ}$ and 764 mm.		

Calculated for Tetraphenylazine.		Found.			
$C_{28}H_{20}N_2$		I.	II.	III.	IV.
Carbon	87.50	88.49	88.30	88.45	.....
Hydrogen	5.21	5.02	4.99	4.71	.....
Nitrogen	7.29	.....	.....	.....	7.68

The melting point of tetraphenylazine as given by Japp and Wilson is  $246^{\circ}$ ; the melting point as obtained for the body under consideration is  $245^{\circ}$  (uncorrected).

The molecular weight determination was made by the Raoult method, using benzene as the solvent. A Beckmann thermometer, graduated to  $0.01^{\circ}$ , was used, with the well-known Beckman apparatus. The results were as follows :

$$\begin{aligned}
 L &= 21.8262 \\
 C &= 0.162 \\
 P_{100} &= 27.38 \\
 \text{Hence } CL &= 3.5358 \\
 A &= 0.1291 \\
 M &= 379.5 \\
 \text{Calculated for } C_{28}H_{20}N_2 &= 384
 \end{aligned}$$

With concentrated sulphuric acid this body gives a beautiful red color, a very characteristic reaction for tetraphenylazine.

An analysis of the gas from one of the tubes in which the benzoin and malonamide had been heated, showed twenty-nine per cent. of ammonia.

*b. Oxamide and Benzoin.*—Oxamide and benzoin were heated together in molecular proportions at about 200°. The reaction at times took place with violent explosions and appeared to require a temperature of 200°, as below this repeated attempts failed to produce any change. The bodies obtained were separated by the method already described. They were identical with those yielded by malonamide. One of them melted at 244°, gave a red color with concentrated sulphuric acid, and crystallized from chloroform in prisms of the usual form. A molecular weight determination was as follows :

$$\begin{aligned} L &= 20.5973 \\ C &= 0.201 \\ P\ 100 &= 29.19 \\ \text{Hence } CL &= 4.1400 \\ A &= .1418 \\ M &= 345.6 \\ C_4N_2(C_6H_5)_4 &= 384 \end{aligned}$$

The other body gave an indefinite melting point from 193°-217°. Repeated crystallization failed to produce any body with a definite melting point.

I. 0.1073 gram burned with copper oxide gave 5.1 cc. nitrogen at 23° and 766.5 mm. = 5.39 per cent. nitrogen.

II. 0.1005 gram gave 4.9 cc. nitrogen at 25° and 763 mm. = 5.44 per cent. nitrogen.

Analyses of samples of gas from the tubes showed from twenty-five to thirty-three per cent. of free ammonia.

*c. Succinamide and Benzoin.*—Benzoin and succinamide were heated in molecular proportions at 200° for thirty-five hours. When the contents of the tube were treated in the usual way no unchanged succinamide remained, showing a complete decomposition. From the chloroform solution the same body separated in the usual crystalline form, melting at 245° and giving a deep red color with sulphuric acid. A molecular weight determination gave the following results :

$$\begin{aligned}
 L &= 17.9414 \\
 C &= 0.175 \\
 P_{100} &= 27.73 \\
 \text{Hence CL} &= 3.1397 \\
 A &= 0.1381 \\
 M &= 354 + \\
 C_4N_2(C_6H_5)_4 &= 384
 \end{aligned}$$

From the alcoholic filtrates white crystals were obtained melting from  $192^{\circ}$ – $207^{\circ}$ , with in one instance a small portion not melting until  $216^{\circ}$ . The analysis gave the following.

0.1033 gram burned with copper oxide gave 5.9 cc. nitrogen at  $26.5^{\circ}$  and 761 mm. = 6.32 per cent nitrogen.

It will be noticed that this analysis shows a considerable difference from that of the similar body obtained from oxamide. This is another reason for supposing this body to be a mixture of benzoïniam and benzoïnidam. The former has the formula  $C_{10}H_{12}N_2O$ , giving 6.93 per cent. nitrogen and melting at "temperatures varying from  $190^{\circ}$ – $220^{\circ}$ , according as the temperature was raised slowly or rapidly." The latter has the formula  $C_{10}H_{12}NO$ , giving 3.45 per cent. nitrogen, and melting at  $199^{\circ}$ . That a mixture of these two bodies would give the results obtained as mentioned above, is natural. In the work of Japp and Wilson sufficient alcohol was put in the tubes to hold in solution much of the material produced, and hence the two bodies were separated. In the reactions, as carried out with the acid amides, the pressure of the evolved gases was so great that but little alcohol could be used. Hence only a small amount of the material produced was held in solution by the alcohol. This fully accounts for the non-separation of the two bodies by the method described by Japp and Wilson.

In order to compare the bodies obtained by the action of the amides upon benzoïn with those obtained by the method as described by Japp and Wilson, benzoïn was heated in sealed tubes with alcoholic ammonia. One tube was heated at  $150^{\circ}$ – $180^{\circ}$  for eight hours. The contents were then examined in the usual way and by means of the melting point tetraphenylazine was found to have been formed, together with a body melting finally at  $210^{\circ}$ , but softening much below this. A second tube,

heated at  $200^{\circ}$  for several hours, also showed the formation of tetraphenylazine, but only very slight traces of any body melting at about  $200^{\circ}$ . But what was doubtless lophine was found in considerable amount, as shown by the isolation of a body melting at  $272^{\circ}$ . These reactions indicate that at higher temperatures lophine is produced, while at lower temperatures benzoinam is obtained in larger amount. This conclusion is strengthened by the observation that with only one amide was any lophine detected. This was with benzamide, which did not react with benzoin, except at temperatures much above those used with the other amides. It is true that the temperature at which the other amides react without producing lophine was equal to or even above that at which lophine was formed by the direct action of alcoholic ammonia. But this could be caused by the greater heat required for the breaking down of the amides. It seems quite possible that this might offer a means of studying the constitution of benzoinam.

*d. Acetamide and Benzoin.*—Benzoin and acetamide, in molecular proportions, heated together at  $150^{\circ}$  for four hours, did not react. Further heating at  $190^{\circ}$ – $210^{\circ}$  for six hours was also without effect. In a second tube the amount of acetamide was doubled and the tube heated for six hours at  $150^{\circ}$ , without any reaction taking place. In the next experiment four times the molecular quantity of acetamide was used for the benzoin employed, making about two grams of each and the tube was heated at  $190^{\circ}$ – $210^{\circ}$  for nearly six hours. When opened the odor of ethyl acetate was very evident, and an examination of the material showed that a reaction had taken place. Another tube with four grams of each was then heated at  $190^{\circ}$ – $200^{\circ}$  for six hours. When opened the odor proved both ethyl acetate and ammonia to be present. By means of repeated boilings with alcohol the usual bodies were separated and identified.

The tetraphenylazine melted at  $242^{\circ}$ , gave a deep red color with concentrated sulphuric acid, and crystallized from chloroform in the usual prismatic crystals. From the earlier alcoholic extracts bodies were obtained, melting at  $192^{\circ}$ – $194^{\circ}$  and  $206^{\circ}$ – $209^{\circ}$ . The yields were very small; but these observations would indicate that the reaction had taken place in the same manner as shown before.



*c. Butyramide and Benzoïn.*—Butyramide was prepared by the method of Hofmann.<sup>1</sup>

In the first experiment 0.8 gram of the butyramide was heated with one gram of benzoïn at 200° for six hours. No action took place. The tube was then heated for six hours at 250°; when opened the odor of ammonia was strong, and an ethereal odor was readily detected. A second tube, with double the above quantities of material, was then heated for eight hours at 200°, and for four hours at 220°. The contents of the two tubes were united and worked up as before with the usual results. The tetraphenylazine melted at 246°, gave an intense red color with sulphuric acid, and crystallized from chloroform in the usual prismatic form. The body soluble in alcohol melted at 193°–205°. In this instance the tetraphenylazine did not appear to be the principal product of reaction, as it was produced in much less amount than the lower melting body. This differs very decidedly from the usual reaction. The yields were small.

*f. Valeramide and Benzoïn.*—In the first experiment with benzoïn and valeramide one gram of each was used and the tube heated four hours at 200°. As no action had taken place it was then heated for several hours at temperatures varying from 230°–280°. When opened the usual combination of ammoniacal and ethereal odors was observed. Examinations of the small amount of product showed that a reaction had taken place.

To obtain more of the substance two more tubes, with larger amounts of material, were heated for several hours at from 220°–270°, until a change was evident. The contents of the three tubes were then worked up as before with the usual results. The yield obtained was very small, but tetraphenylazine was identified by the melting point of 246°, the red color with sulphuric acid and the crystalline form. The other body melted at 193°–209°. As with butyramide, the relative proportion of the products was different from that observed with the amides of the dibasic acids, tetraphenylazine being produced in smaller amount than the other body.

### III. ACTION OF THE AMIDES OF THE AROMATIC SERIES UPON BENZOIN.

*a. Benzamide and Benzoïn.*—Molecular proportions of benzoïn

<sup>1</sup> Ber. d. chem. Ges., 15, 981.

and benzamide were first heated together in an oil-bath at  $120^{\circ}$ . No action took place. The tube was then heated at  $150^{\circ}$ – $160^{\circ}$ . Examination of the tube contents showed unchanged benzoin and benzamide and nothing else. A second tube, with the same amount of material (two grams of benzoin), was heated for six hours at  $190^{\circ}$ – $200^{\circ}$ , but without producing any reaction. Another tube, with double the amount of benzamide heated at  $190^{\circ}$ – $200^{\circ}$  for several hours, gave the same results, unchanged benzoin and benzamide being found, without anything else.

As these experiments had shown that benzamide would not react with benzoin under the same conditions that the other amides did, further trials were made at higher temperatures, with better results. The first tube prepared with the amount of alcohol which had usually been used were all lost by explosion, at temperatures between  $220^{\circ}$  and  $250^{\circ}$ . The next tube prepared contained only a very small amount of alcohol with benzoin and benzamide in the molecular proportions of 1 to 2. It was first heated four hours at  $250^{\circ}$  without producing any change. A second heating for seven hours at  $250^{\circ}$ – $260^{\circ}$  was also without apparent action. Then for seven hours the tube was heated at  $290^{\circ}$ – $300^{\circ}$ , a portion of the time the temperature even rising to  $360^{\circ}$ . When the tube was opened there was no pressure apparent, the odor of ammonia was but slight, but the alkaline reaction of the liquid was strong. The yield of crystals obtained was very small, but melting point determinations showed that a change had taken place, with indications of the production of tetraphenylazine and of some body with a higher melting point.

Another tube, prepared in the same way, was heated for seven hours at  $250^{\circ}$ – $265^{\circ}$ . As the crystals were deposited on cooling, the tube was opened and the contents examined. The yield was very small, but separation in the usual way, by means of boiling alcohol and chloroform, showed the formation of at least two bodies, which from their melting points indicated lophine and tetraphenylazine. There was no indication whatever of the presence of the bodies with melting points of about  $200^{\circ}$  and which were found as a part of the products of reaction of all the other amides with benzoin. As the only different condition

here was that of higher temperature, the same conclusion is reached that was pointed to with the experiments with alcoholic ammonia and benzoïn, *i. e.*, the higher the temperature of reaction the less the amount of benzoinam and the greater the amount of lophine which is formed.

*b. Salicylamide and Benzoïn.*—When heated together in the proportion of two molecules of salicylamide to one of benzoïn, for six hours at  $200^{\circ}$ , the reaction was easily induced. When the tube was opened a slight pressure was evident, the liquid had a faintly alkaline reaction, but no odor of ammonia, while that of a salicylic ester was very noticeable. An examination of the crystals obtained from the tube was made in the usual way by means of treatment with boiling alcohol and chloroform.

Tetraphenylazine was found and identified by its melting point, color reaction with sulphuric acid and crystalline form. From the alcoholic extracts the usual body separated, with melting points varying from  $192^{\circ}$ – $207^{\circ}$ . Salicylamide therefore reacted just as the fatty amide did. About one-fifth of the original amide used was found unchanged in the liquid drained from the crystals in the tube.

In order to determine whether the amides would react with benzoïn directly, without the intervention of a solvent, experiments were tried by heating them together in a dry condition.

When malonamide and benzoïn were mixed together and heated by means of a paraffine bath at about  $160^{\circ}$ , action commenced and there was an evolution of gas, which proved to be ammonia. At  $170^{\circ}$ , the melting point of malonamide, the effervescence was very rapid. The heating was continued until the reaction had about ceased, and, on cooling, the reddish crystalline mass was boiled with alcohol and the residue dissolved in chloroform. The melting point determinations showed that tetraphenylazine had been produced, with slight traces of benzoinam.

Succinamide, when heated with benzoïn in the same way, was also found to react with the evolution of ammonia. Benzamide, even when heated to  $200^{\circ}$  with benzoïn, under the same conditions, was without action. These results are entirely in accord with those obtained in the presence of alcohol, and under pressure.

## IV. THEORETICAL DEDUCTIONS.

Although in the nature of a repetition, the results of this work with amides may be summed up as follows:

Acid amides, heated with benzoin in alcoholic solution, do not yield condensation products in the true sense of the term, but break down with the liberation of ammonia and the formation of an ester with the alcohol. The ammonia then reacts with the benzoin in the way already studied by others.<sup>1</sup> This reaction takes place with the greatest ease with malonamide, and only with great difficulty and at high temperatures with benzamide. In every case tetraphenylazine is a constant product, while benzoinam and benzoinidam are produced at lower temperatures, lophine at higher. The presence of alcohol is not necessary to induce the breaking down of the amide, as the same results are obtained by the simple interaction of the dry materials. The great difference between the reactions of benzamide and of salicylamide is of interest as another example of the weakening of the benzene ring by the presence of hydroxyl in the nucleus of the latter.

## V. A STUDY OF TETRAPHENYLAZINE.

*a. Historical.*—As tetraphenylazine was found to be the chief product of the action of amides upon benzoin, a further study of this body was instituted.

A brief review of what has been done in its preparation and investigation may be of interest. Laurent studied<sup>2</sup> the action of ammonia on benzoin. Later Erdmann<sup>3</sup> took up the same study and gave the name benzoinimide to what has since been shown to be tetraphenylazine by Japp, Wilson<sup>4</sup> and Burton. The very interesting work of these later investigators showed, that on distillation with lime, the so-called benzoinimide of Erdmann was converted into diphenanthyleneazotide, as it was then called. Ammonia acting on  $\beta$ -naphthoquinone was shown to produce  $\alpha\beta$ -naphthazine, a body whose constitution had been already proved through its syntheses by Witt<sup>5</sup> by the condensa-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ann. Chem. (Liebig)*, 66, 181. and *Jab. Phys. Wiss.*, 18, 354, and 26, 666.

<sup>3</sup> *Ann. Chem. (Liebig)*, 135, 181.

<sup>4</sup> *J. Chem. Soc.*, 49, 825 and 843, and 51, 98.

<sup>5</sup> *Ber. d. chem. Ges.*, 19, 2794.

tion of  $\beta$ -naphthoquinone with  $\alpha\beta$ -diamidonaphthalene. As ammonia acting on phenanthraquinone yields the "diphenanthyleneazotide" this was also considered an azine, tetraphenyleneazine, and hence the so-called ditolaneazotide, which by distillation with lime yields the tetraphenyleneazine, was itself given the proper name tetraphenylazine.

Braun and Meyer<sup>1</sup> have produced this same body by the action of sodium amalgam on benziloxime, and have called it tetraphenylaldine. The only substitution product of tetraphenylazine which has been obtained is the tetra-nitro derivative prepared by Braun and Meyer. Attempts were, therefore, made to obtain bromine and chlorine derivatives, but, as the results will show, without success.

To obtain the material for study, the tetraphenylazine was prepared by the method described by Japp and Wilson, by heating benzoïn with ammonium acetate in an open flask, and separating the azine from the other products of the reaction by means of alcoholic hydrochloric acid. This was found to be an entirely satisfactory method and gave a good yield of pure material, melting at  $245^{\circ}$ .

*b. Bromination.*—The azine was first heated with carbon bisulphide and an excess of bromine for eleven hours on the water-bath with return condenser. Acid vapors were given off in slight amount. An examination of the material showed that no bromination had taken place, the azine being found unchanged, melting at  $245^{\circ}$ . A second experiment was made by boiling a solution of the azine in strong alcoholic hydrochloric acid with bromine. An examination of the material showed that the azine was unaffected.

In the third experiment, chloroform was used as the solvent and bromine was added in the calculated quantity to produce a tetra-brom substitution product. Acid vapors were given off and the separation of dark red crystals appeared to indicate that a substitution had taken place. These, on exposure to air, rapidly lost their color, and by treatment with alcohol yielded the unchanged azine, as shown by the melting point and the absence of any halogen. Some of the reactions, as the action

<sup>1</sup> *Ber. d. chem. Ges.*, 21, 1269.

toward solvents, seemed to indicate that an unstable addition product might have been formed, but it is more probable that the red crystals represented simply a mechanical mixture of bromine with the azine. A repetition of the above, with the addition of a few crystals of iodine, gave the same results.

In the next trial some of the azine was heated in a sealed tube with bromine, a crystal of iodine and alcohol for seven hours at  $200^{\circ}$ – $220^{\circ}$ . When the contents were examined it was found that ethyl bromide and acetic acid had been formed, but that the azine was not brominated. The ethyl bromide was identified by its boiling point ( $38^{\circ}$ – $40^{\circ}$ ) and odor, and the acetic acid by its boiling point ( $115^{\circ}$ – $123^{\circ}$ ), and the formation of acetic ether with alcohol and sulphuric acid. The dark residue, when extracted with chloroform, gave the unchanged azine, melting at  $244^{\circ}$ . The insoluble black residue appeared to be carbon, not melting at  $300^{\circ}$ , insoluble in acids, alkalies or the usual solvents, burning with glowing, and not containing any halogen.

*c. Chlorination.*—Tetraphenylazine was dissolved in chloroform, and through the solution contained in a retort placed on the water-bath and connected with a return condenser, a stream of dry chlorine gas was passed for six hours. An examination of the material showed that no change had taken place. The same material was then subjected to the action of chlorine again, for the same length of time, with the same result. Aluminum chloride was then added to the contents of the retort and a rapid stream of chlorine was passed through for six hours, for a part of this time the retort being in direct sunlight. The residue, after removal of the solvent, was boiled with water, well washed, dried, and dissolved in chloroform. An examination of the material showed that no halogen had entered the body. Hence neither bromine nor chlorine substitution products could be obtained by the action of the halogens on tetraphenylazine. This great stability of the phenyl groups in the azine ring is of interest, and entirely in accord with analogy.

*d. Nitration and Amidation.*—Following the method employed by Braun and Meyer<sup>1</sup>, the tetranitro derivative of tetraphenylazine was prepared by slowly adding the azine to cold, fuming

<sup>1</sup> *Loc. cit.*

nitric acid, with stirring. The deep yellow liquid was then poured into an excess of cold water, and the resulting voluminous light yellow powder filtered out, washed, and dried. It has an indefinite melting point between  $140^{\circ}$  and  $150^{\circ}$ . With concentrated sulphuric acid it gives an orange yellow color, very different from the brilliant red yielded by the unchanged azine.

To prepare the amido derivatives, the tetranitroazine was reduced with tin and hydrochloric acid. The clear red solution was diluted with water and the tin removed with hydrogen sulphide. The removal of the last portions of tin was extremely difficult, as not until repeated treatment with the hydrogen sulphide in a nearly neutral boiling solution could a base be obtained free from ash. When the filtrate from the sulphide of tin was made alkaline with ammonia an abundant yellow precipitate was obtained. During the filtration a portion of this appeared to undergo oxidation, as the precipitate, at first yellow, became green on the surface, and the filtrate, at first clear, became turbid on standing. The well-washed precipitate finally ceased to give a turbid filtrate and dissolved in hydrochloric acid with red color. Hydrogen sulphide, when passed into this solution, gave no precipitate. The solution was boiled, to remove the hydrogen sulphide, and made alkaline with ammonia, when a yellow precipitate was thrown down, which when filtered and washed, showed no change of color and gave a clear filtrate. When dried this base is of a brownish yellow color, is slightly soluble in chloroform, more readily in boiling alcohol. From the latter solution, on evaporation, it is obtained as before, in an amorphous condition without any sign of crystallization. When heated it darkens and melts above  $260^{\circ}$ , with decomposition and a slight sublimation.

To determine its composition, the hydrochloride was prepared by dissolving some of the base in dilute hydrochloric acid and evaporating the solution over sulphuric acid in a vacuum desiccator. No crystals could be obtained, but the material dried to a reddish-brown, transparent mass. It melts at about  $140^{\circ}$ , and is readily soluble in water. When the material, which had been dried over sulphuric acid, was heated to  $100^{\circ}$  in the air-bath, its

loss in weight would indicate five molecules of water of crystallization.

0.2867 gram, after heating at  $100^{\circ}$ , weighed 0.2480 gram = 13.49 per cent. water.

$C_4N_4(C_6H_5NH_2HCl)_4 + 5H_2O = 13.23$  per cent. water.

0.2480 gram hydrochloride, dried at  $100^{\circ}$ , gave 0.2243 gram AgCl.

Calculated for  
 $C_4N_4(C_6H_5NH_2HCl)_4$ .  
24.06 per cent. chlorine.

Found.  
22.33 per cent. chlorine.

Platinic chloride, added to the aqueous solution of the hydrochloride, precipitates on standing a reddish-brown double salt.

0.1090 gram platinum double salt gave 0.0325 gram platinum = 29.81 per cent. platinum.

This corresponds to a salt of the composition :

$(C_4N_4(C_6H_5NH_2HCl)_4)_2PtCl_6 + 11H_2O = 30.01$  per cent. platinum.

The filtrate mentioned before as obtained from the precipitation of the base by ammonia becomes turbid on standing and slowly precipitates a dark greenish-blue material. When acidified with hydrochloric acid it gives a dark green solution, which, under certain conditions of dilution, gives a deep blue color. This, when treated with hydrogen sulphide or zinc and hydrochloric acid, changes to green and finally to a yellow color. Standing exposed to the air, it gradually reverts to the blue color, while heating with nitric acid quickly produces the same change.

All these reactions indicate the presence of another base, possibly of two others of different composition. Their constitution was not further investigated.

*e. Crystallographic and Optical Investigation.*—As tetraphenylazine crystallizes from chloroform in brilliant prismatic crystals, an examination of the crystallographic and optical constants was made with the following results :

#### SYSTEM TRICLINIC.

$a : b : c = 0.941^{\circ} : 1 : 0.5611$ .

$\alpha = 83^{\circ} 48' \quad \beta = 85^{\circ} 13' \quad \gamma = 101^{\circ} 38'$ .

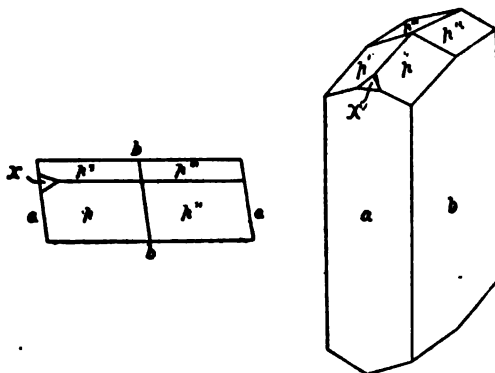
$100 \wedge 010 = 101^{\circ} 13' \quad 1P \wedge 010 = 72^{\circ} 36'$ .

Calculated  $001 \wedge 010 = 86^{\circ} 20' \quad 001 \wedge 100 = 84^{\circ} 36'$ .



## FORMS.

a (100 i- $\bar{1}$ )	p (III P')	p <sub>2</sub> (III $\bar{1}$ P)
b (010 i- $\bar{1}$ )	p <sub>1</sub> (II $\bar{1}$ 'P)	p <sub>2</sub> (II $\bar{1}$ P')
x (405 $\frac{1}{2}$ - $\bar{1}$ )		



## OBSERVED ANGLES.

ab = 101° 13'	b <sub>1</sub> p <sub>1</sub> = 80° 4'	p <sub>2</sub> p <sub>2</sub> = 26° 35'
bp = 72° 36'	ap = 68° 47'	p <sub>2</sub> p = 35° 33'
bp <sub>2</sub> = 79° 23'	ap <sub>1</sub> = 73° 12'	p.p = 26° 30'
b <sub>1</sub> p <sub>2</sub> = 73° 16'	pp <sub>2</sub> = 35° 2'	ax = 55° 42'

Crystals flat, tabular parallel to 010.

Cleavage none.

Optically negative, as determined by a quarter undulation mica plate.

Plane of optic axes parallel to c.

Apparant axial angle  $2E = 18^\circ$ .

## EXTINCTION ANGLES.

On b..... parallel to edge ab.

On a..... parallel to edge ab.

On section normal to c = 14° with b.

Indices of refraction determined by the microscope method, using sodium light.

On b with edge ab normal to principal section of Nicol	= 1.873
" " " " parallel " "	" = 2.217
On a " " " normal " "	" = 1.946
" " " " parallel " "	" = 1.897

## VI. ACTION OF BENZOIN UPON UREA AND THIOUREA.

While studying the action of amides with benzoïn, the reac-

(2)

tions with urea and thiourea were examined. Not until after considerable work had been done was it found that Anschütz and Gelderman<sup>1</sup> had previously studied these reactions and published their conclusions. The results that were obtained fully corroborated those of these chemists, and so will not be given in detail.

*a. Urea and Benzoin.*—Urea and benzoin, when heated together with alcohol in sealed tubes at 175°–195°, do not react as the true amides do, but form condensation products, with the elimination of water. That they react in this manner is to be accounted for by the fact that the two amido groups are both linked to the same carbon atom. It would be interesting to see whether the amides of the amido acids of the fatty and aromatic series would undergo condensations of the same nature.

The body obtained by the condensation of urea and benzoin dissolves in boiling alcohol, with a beautiful blue fluorescence, and crystallizes in prismatic forms, which are dichroic. In the earlier work on these substances, it was found that under certain conditions this body is dimorphous, coming out from solution in two entirely distinct forms, one prismatic, as just mentioned, and the other in bunches of very delicate white needles. When the two forms were very carefully mechanically separated and dissolved in boiling alcohol, each solution, on cooling, showed crystals of both forms. The tendency was toward the assumption of the prismatic form. All attempts at ascertaining the conditions under which these could be produced were fruitless. Later work failed to give the needle form, only the prisms being obtained. That the two bodies were identical was shown by the melting points and a determination of the nitrogen content. Both softened at about 280° and melted, not sharply, at about 318°. Analyses gave the following results :

NEEDLE FORM.

0.1023 gram substance, burned with copper oxide, gave 11.4 cc. nitrogen at 23° and 763 mm. = 12.59 per cent. nitrogen.

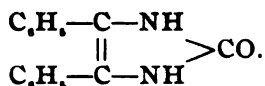
PRISMATIC FORM.

0.2022 gram gave 23.5 cc. nitrogen at 23° and 759.5 mm. = 12.70 per cent. nitrogen.

<sup>1</sup> *Loc. cit.*

The two bodies are therefore identical.

Extended study by Anschütz, Gelderman, and Schwickerath<sup>1</sup> has shown this body to be diphenylacetylenurein.



Analysis of the prismatic crystals mentioned above confirm this.

0.2203 gram substance gave 0.1044 gram water, and 0.6123 gram carbon dioxide.

	Calculated for $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}$ .	Found.
Carbon .....	76.27	75.77
Hydrogen .....	5.09	5.26
Nitrogen .....	11.86	12.70
Oxygen .....	6.78	

Evans<sup>2</sup> has shown that condensations of urea with  $\beta$ -diketones can be induced by the influence of acids on their alcohol solution. Similar experiments were therefore tried with urea and benzoïn. Urea was added to a saturated alcoholic solution of benzoïn, and different amounts of concentrated hydrochloric acid added. No condensation was, however, produced.

*b. Thiourea and Benzoïn.*—The thiourea used was prepared from ammonium thiocyanate. When heated with benzoïn a condensation takes place, with the formation of what Anschütz and Schwickerath have shown to be  $\alpha\beta$ -diphenylglyoxaline sulphhydrate. In the experiments with this body the two forms of crystals, as mentioned under the urea derivative, were produced, but the prismatic form was in very much the greater quantity, the needle form being only observed in very small amount. An attempt at producing the needle form in larger amount was made by using, instead of thiourea alone, a mixture of equal parts of this and ammonium thiocyanate. The results, however, were the same, only traces of the needle form appearing. This confirms the work of Anschütz, who found that the same body was produced whether thiourea or ammonium thiocyanate was used.

<sup>1</sup> *Loc. cit.*, and *Ann. Chem.* (Liebig), 284, 8.

<sup>2</sup> *J. prakt. Chem.*, 48, 489.

## ON THE INVERSION OF SUGAR BY SALTS.

By J. H. LONG.

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It is a well known fact that the specific rotation of solutions of cane sugar is decreased by the presence of many neutral salts, even by sodium chloride and other salts of the alkali and earth groups. The amount of this decrease has been measured by several chemists, and recently very carefully by K. Farnsteiner,<sup>1</sup> who has noted the connection between the molecular weights of the salts dissolved with the sugar and the amount of the depression they produced. In a solution containing for each part of sugar three parts of water and 1.0036 parts of sodium chloride the specific rotation dropped from  $66.6^\circ$  to  $62.47^\circ$ . Similar effects were observed in other cases.

The extent of this depression is dependent to some degree on the temperature, but a temporary increase in temperature does not permanently alter the rotation. In illustration, a solution of pure saccharose containing in 100 cc. twenty-five grams of the sugar and ten grams of potassium nitrate gave a specific rotation of  $\alpha_D = 66.22^\circ$  at  $20^\circ$ . After heating one hour, but so as to avoid evaporation or pressure, the rotation was again determined and found to be practically the same. The solution was heated in a small flask closed with a perforated rubber stopper having a capillary glass tube in the perforation. It was possible by this means to heat the liquid to  $100^\circ$  in boiling water without risk of appreciable loss by evaporation.

On the other hand, a solution of sugar and zinc sulphate which gave a specific rotation of  $64.98^\circ$  when fresh, showed, after having been heated forty-five minutes in boiling water, as before, a specific rotation of  $36.84^\circ$ . In this case a decided inversion had taken place, as easily shown by other tests. The behavior of zinc sulphate is similar to that of a large number of other substances. Loewenthal and Lenssen<sup>2</sup> state that zinc sulphate and other neutral salts are without inverting action, but Béchamp, a little later<sup>3</sup> gave a list of these salts which are able to produce a marked inversion. The phenomenon is an inter-

<sup>1</sup> *Ber. d. chem. Ges.*, 23, 3570.

<sup>2</sup> *Jsb. Chem.*, 1863, 120, and Ostwald, *Allg. Chemie*, 2, 811.

<sup>3</sup> *Jsb. Chem.*, 1864, 573, and Gmelin, *Handbuch der Org. Chem.*, iv., 1, 691.

esting one, and one which can now be easily explained, but until quite recently the literature has been almost silent on the subject. I wish to present in what follows a few observations bearing on the question.

Over a year ago in giving instruction to a class of students in the use of the polarimeter I suggested, as an illustration of a substance for examination, not free from color, the syrup of ferrous iodide of the pharmacopeia. Instead of exhibiting a more or less marked right hand rotation, as was expected, it was found to be strongly levo-rotatory. The syrup, however, was known to be old and had been exposed to the light. As a certain practical interest attaches to the question it was decided to investigate fresh solutions.

The syrup of the pharmacopeia is made to contain in 100 cc. about 63 grams of sugar and 13.4 grams of ferrous iodide. On January 19, 1895, a liter of this solution was made according to the usual process, special care, however, being taken in the selection of the sugar and iodine employed. The liquid polarized immediately, in a 200 mm. tube, gave  $\alpha_D = 81.15^\circ$  at  $20^\circ$ . Four days later the rotation was found practically unchanged, the syrup having been kept meanwhile in the dark. A bottle holding about 100 cc. and furnished with a glass stopper was then filled with the syrup and allowed to stand until May 6th and exposed to diffused light. This portion now showed on polarization  $\alpha_D = 53.12^\circ$  in the 200 mm. tube, while the original, kept in the dark, polarized  $63.17^\circ$ . On this date, May 6th, a second portion of the original was filled into a bottle and allowed to stand in the light. It was polarized at different intervals, with results as follows, at  $20^\circ$ , in the 100 mm. tube :

July 15th	$\alpha_D$ .....	+6.66°
Aug. 24th	" .....	-4.36°
Oct. 22nd	" .....	-13.10°
Nov. 15th	" .....	-13.42°

Another portion of the original which had stood since January 19th in a small full bottle in the light gave now in the 100 mm. tube  $\alpha_D = -15.66^\circ$ . From this it appears that in the interval the saccharose had undergone complete inversion. The original rotation observed,  $81.15^\circ$ , was that of a solution in which some inversion had already taken place.

Another solution was prepared on May 9th, containing in 250 cc. 140 grams of sugar and an amount of ferrous iodide corresponding to twenty-eight grams of iodine. The syrup and iodide solution were hot when mixed. This polarized at  $20^{\circ}$  gave a rotation of  $33.25^{\circ}$  in the 100 mm. tube, which corresponds to a specific rotation of  $59.38^{\circ}$ . At intervals the following rotations were found from two portions of this solution, which had been poured into glass stoppered bottles and kept in the light. One bottle was full and the other not quite full.

		Full bottle.	Partly filled.
July 13th	$\alpha_D$ .....	$18.66^{\circ}$	$+9.30^{\circ}$
Aug. 24th	" .....	$8.58^{\circ}$	$+3.56^{\circ}$
Oct. 22nd	" .....	$3.76^{\circ}$	$-10.16^{\circ}$
Nov. 15th	" .....	$2.70^{\circ}$	$-10.75^{\circ}$

It is apparent from the above that the presence of air in the bottle with the solution has a marked influence on the rapidity of inversion.

#### INFLUENCE OF TEMPERATURE.

The solution just described stood at the laboratory temperature during the time of the observations. A marked decrease in the time required for full inversion would naturally be expected by working at a higher temperature. This was shown by heating some of the last solution in boiling water during ninety minutes. The solution was contained in a flask with a capillary stopper. Before heating it had a rotation of  $33.25^{\circ}$  in the 100 mm. tube; after the application of heat the reading was  $-12.75^{\circ}$  in the same tube. The following day the solution was reheated through three hours and polarized again, giving now  $-13.00^{\circ}$  at  $20^{\circ}$ . Heating through ninety minutes was therefore sufficient to complete the reaction, and it is evident that an inversion which at the mean laboratory temperature of  $20^{\circ}$ - $25^{\circ}$  requires months for its completion may be accomplished in less than two hours at the temperature of boiling water.

It was found later that a moderate increase of temperature does not greatly hasten the inversion; this becomes rapid only above  $60^{\circ}$ .

#### INFLUENCE OF LIGHT.

It should be remarked that the inversion by heat, as well as

by long standing in the light, is accompanied by a decided loss of color. A solution of ferrous iodide exposed to the air, or protected from the air and kept in the dark, soon becomes brown from partial decomposition and separation of iodine, which is easily shown by the starch reaction. In stoppered bottles in the light, however, this decomposition is almost wholly prevented and in an already colored solution in which free iodine is shown by tests, the color is lost by exposure to the light.

Well-made undecomposed solutions of ferrous iodide are described as light green, but they may become almost as colorless as water, leaving the iron in a perfectly reduced condition. It has been found by numerous trials that the rate of inversion is more rapid in bottles exposed to the light than in similarly filled bottles kept in the dark. The rapidity of inversion is further increased if the solution is exposed to the action of light and heat together. More will be said of this later.

The phenomena described above are not confined to ferrous iodide but are exhibited by many other salts. In fact, from theoretical considerations, they should be expected in some degree from the salts of all the so-called heavy metals, as will presently be pointed out. First, however, some actual experimental results will be given.

#### FERROUS CHLORIDE.

A solution containing in 100 cc., 50 grams of cane sugar and four and one-tenth grams of pure ferrous chloride was prepared. The ferrous salt was made by the action of an excess of iron on hydrochloric acid, and the syrup made with this and the sugar was bright green. It showed a rotation of  $32.75^\circ$  in the 100 mm. tube, or a specific rotation of  $65.50^\circ$ . After heating one hour to  $100^\circ$  the rotation was found to be  $-6.42^\circ$  in the same tube.

#### FERROUS BROMIDE.

The solution contained in 100 cc., 50 grams of saccharose and ten grams of the bromide. The latter was made by the action of bromine and water on iron, and the solution so obtained was filtered into the dissolved sugar. The rotation of the fresh mixture was found to be  $32.25^\circ$ . A portion was heated one hour to  $100^\circ$  and was then polarized, after cooling to  $20^\circ$ , giving now a rotation of  $-10.26^\circ$ .

## FERROUS SULPHATE.

The solution of 100 cc. was made with fifty grams of sugar and ten grams of pure crystallized sulphate. It was slightly cloudy and could not be polarized with the greatest accuracy, but the reading was nearly  $33^\circ$ . A portion was heated one hour away from the air. It became clear and could be easily examined in the polarimeter, showing now at  $20^\circ$  in the 100 mm. tube  $18.20^\circ$ . This decrease is much less than in the other cases, but not unexpected.

## FERROUS AMMONIUM SULPHATE.

The solution made contained in 100 cc., fifty grams of sugar and ten grams of the crystallized salt. When fresh it gave a rotation of  $33.08^\circ$ . After heating five hours to  $71^\circ$  the rotation was found to be  $27.20^\circ$ . This solution was allowed to stand in a stoppered bottle in the light and was polarized at different intervals with the following results:

July 24th	$a_D$ .....	$27.20^\circ$
Aug. 24th	" .....	$20.22^\circ$
Oct. 22nd	" .....	$10.23^\circ$
Nov. 15th	" .....	$7.53^\circ$

We have here, as before, a slow rate of inversion.

## MANGANOUS CHLORIDE.

A solution was made on July 24th, containing in 100 cc. fifty grams of sugar and ten grams of the carefully purified salt with  $4H_2O$ . It gave immediately a rotation of  $32.88^\circ$ , and after heating five hours to  $71^\circ$  a rotation of  $28.16^\circ$ . From this date, July 24th, the heated portion was allowed to stand in the light at the laboratory temperature in a full bottle, and showed at intervals the following rotations, all in the 100 mm. tube, at  $20^\circ$ :

Aug. 24th	$a_D$ .....	$22.20^\circ$
Oct. 22nd	" .....	$4.71^\circ$
Nov. 15th	" .....	$1.66^\circ$

After standing a short time in the light this solution became as colorless as water when observed in a clear glass bottle of four cm. diameter.

## MANGANOUS SULPHATE.

The experimental solution was made to contain in 100 cc. fifty



grams of sugar and ten grams of crystallized manganous sulphate ( $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ). The rotation was found to be  $33.16^\circ$ . On heating the solution one hour to  $100^\circ$  it became slightly decomposed and darker in color, instead of lighter as with the chloride. The decomposition product was small in amount but exceedingly fine and dark. It remained long in suspension, making an exact reading of the rotation impossible. It was about  $+7^\circ$ , however, in the 100 mm. tube. The suspended substance was probably an oxide of manganese.

#### ZINC SULPHATE.

A solution containing fifty grams of sugar and ten grams of the sulphate in 100 cc. showed when fresh a rotation of  $32.98^\circ$  for 100 mm. After heating forty-five minutes in boiling water the rotation was reduced to  $18.42^\circ$  for the same tube.

#### POTASSIUM ALUMINUM SULPHATE.

With a solution containing fifty grams of sugar and five grams of the alum in 100 cc. a rotation of  $33^\circ$  was found immediately. A portion was heated one hour in the water-bath to  $100^\circ$ , and on cooling to  $20^\circ$  was polarized again, showing now a rotation of  $-9.99$ . The heated solution became slightly cloudy, but the original remained clear through the several weeks it was kept.

#### LEAD NITRATE.

A fresh solution with 50 grams of sugar and ten grams of the salt in 100 cc. showed a rotation of  $33.13^\circ$ . A portion heated one hour to  $100^\circ$ , showed, after cooling to  $20^\circ$ , a rotation of  $-9.65^\circ$  in the same tube.

#### LEAD CHLORIDE.

Some chloride was made by precipitation of the nitrate by sodium chloride. The product was recrystallized from hot water and washed repeatedly on a filter with cold water. About two grams of the moist precipitate was mixed with fifty grams of sugar in water enough to make ninety cc. and heated until it dissolved. On cooling the volume was made to 100 cc. A part of the chloride separated. The rotation was now found to be  $23.52^\circ$ . The mixture was shaken and a portion transferred to a flask with capillary stopper, where it was heated one hour to  $100^\circ$ . After cooling the rotation was found to be  $-7.53^\circ$ .

## CADMIUM CHLORIDE.

A fresh solution with fifty grams of sugar and eight grams of the chloride in 100 cc. gave a rotation of  $32.91^{\circ}$ . After heating to  $100^{\circ}$  it was reduced to  $-9.50^{\circ}$ .

## MERCURIC CHLORIDE.

The original solution of fifty grams of sugar and five grams of chloride in 100 cc. gave a rotation of  $33.22^{\circ}$ . A portion was heated an hour to  $100^{\circ}$  and became turbid, depositing on cooling a fine white precipitate. The clear liquid showed a rotation of  $-10.80^{\circ}$ . A second portion was heated a shorter time, to the beginning of turbidity only. It was quickly cooled and polarized, showing a rotation of  $-4.82^{\circ}$ . By prolonged heating more of the precipitate is formed. It appears to consist of mercurous chloride only.

The salts tested above, while commonly called neutral, are those in which the base is very weak when compared with the acid. It is such salts that show in solution an acid reaction with certain indicators and the parallelism between the phenomena observed here and that of the inversion of sugar by acids naturally suggested itself. The following further test with a solution of ferrous iodide was therefore made. This solution contained in 100 cc. fifty grams of sugar and ten grams of the iodide. It polarized when fresh  $32.41^{\circ}$  in the 100 mm. tube. A number of small vials were nearly filled with this solution and they were heated in a thermostat through different times as shown below. The vials were made of selected glass, not readily attacked, and before use were heated some hours with hydrochloric acid. They were then washed and boiled with distilled water and dried. Before being placed in the thermostat they were closed with rubber stoppers having a capillary tube through the perforation. The upper end of this extended above the water in the thermostat. The capillary opening was sufficiently fine to prevent any appreciable evaporation of the syrup while being heated. The water in the thermostat was kept at about  $77.5^{\circ}$ . Vials were removed from time to time and cooled quickly so that the contents could be examined in the polarimeter. The following results were found :

Time of heating in minutes.	Observed rotation.
0	32.41°
30	28.00°
60	26.25°
90	26.15°
210	24.61°
390	18.48°
570	16.60°
810	4.70°

These figures show a rapid, but an irregular change, in the rotation with the time, but as the temperature was not maintained with great accuracy, and as some of the vials were more exposed to the light than others, greater uniformity could not be expected.

To determine whether or not the inversion proceeds according to the law of Wilhelmy, a second series of experiments was made in which the temperature was carefully regulated and in which the small vials holding the sugar solutions were wrapped in tinfoil for protection against the light. The temperature in the last series of experiments was too low to permit them to be completed in a reasonable time. It was therefore brought to 87.5° for the following tests.

The amounts of sugar and ferrous iodide were the same as before, but greater care was taken in the preparation of the solution. Several samples of high grade commercial sugar were tested, and one was selected which satisfied all requirements as to purity. For 250 cc. of solution 125 grams of this sugar is dissolved in a small quantity of water in a graduated flask by aid of heat. Then 20.5 grams of the pure iodine, sublimed with potassium iodide, is weighed out and mixed in a flask with fifty cc. of water and seven grams of pure fine iron wire. The action of the iodine on the iron begins soon and must be checked after a time by dipping the flask in cold water. Finally when the action is practically complete, as shown by the disappearance of the iodine and change of color to greenish brown, the solution is boiled to make the reduction to the ferrous condition perfect. The amount of iron taken is largely in excess of that which can combine with the iodine. The ferrous solution is now allowed to cool to 50°-60° C. and filtered into the cooled sugar

solution made as above. The last traces of iodide from the flask and paper are washed down into the syrup by aid of a little boiled and cooled water. Finally the whole volume is made up to 250 cc. by the addition of distilled water. In this manner a solution is secured which contains in 100 cc., fifty grams of saccharose and ten grams of ferrous iodide, and which is practically free from inversion. The specific rotation of the strong pure syrup is  $66.5^\circ$ ; that prepared with the iodide is  $64.82^\circ$ , as found from the mean of many closely agreeing determinations. It will be noted that this lower specific rotation is about the same as that found for the solutions of the other salts described above. The decrease in the rotation is apparently not a result of inversion.

The method of preparation of the syrup of ferrous iodide as described in the Pharmacopeia leaves a product slightly inverted because of the higher temperature of mixing the sugar and iodide solutions. When portions of the syrup made as just described are heated in boiling water an hour, in flasks with capillary stoppers to prevent evaporation, the rotation is reduced to  $-11.5^\circ$  at  $20^\circ$  for the 100 mm. tube. This value is almost identical with that calculated from the experiments of Gubbe,<sup>1</sup> viz.,  $-11.31^\circ$  for the rotation produced by the inversion of fifty grams of cane sugar in 100 cc. The presence of the excess of iodide seems to be without much influence on the specific rotation of the invert sugar.

In the experiments given below, the rotations were found in a 100 mm. tube at  $20^\circ$ . The reading before heating was  $32.41^\circ$ , and this is taken as the initial rotation instead of the theoretical  $33.25^\circ$ . Applying the Wilhelmy-Ostwald formula we have

$$\text{nat. log. } \frac{A}{A-x} = Ct,$$

in which  $A$  represents the total amount of sugar present and may be measured by the total change in the rotation. It is therefore  $32.41^\circ - -11.5^\circ = 43.91^\circ$ .  $x$  represents the amount of sugar inverted at the time  $t$ , and is measured by the decrease in rotation at that time.  $A-x$  represents the sugar remaining and the velocity of the inversion should be proportional to this.

<sup>1</sup> *Ann. Chem. Phys.* 3, 207

The table below gives the results of a series of experiments. The solutions were warmed two minutes before the counting of the times,  $t$ , began, as this was found necessary to bring them to the proper temperature. This, of course, introduces a small error into the calculation. The values in the fourth column are obtained by the use of common logarithms.

$t$ min.	Observed rotation.	$x$	$\log. \frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
30	28.50°	3.91°	0.04050	0.00135
60	24.85°	7.56°	0.08206	0.00137
120	17.80°	14.61°	0.17569	0.00146
180	13.35°	19.06°	0.24723	0.00137
240	6.32°	26.09°	0.39165	0.00163
300	4.32°	28.09°	0.44335	0.00148
420	-9.00°	41.41°	1.24461	0.00296

The results of the last column are sufficient to indicate that the inversion follows the general law shown by Wilhelmy to hold for the action of weak acids on sugar solutions. The values of  $\frac{1}{t} \log. \frac{A}{A-x}$  are not constant, but considering the conditions of the experiment, must be considered close enough until the last one is reached. The solution of the sugar is a very strong one containing fifty grams in 100 cc., and from such a degree of concentration no great regularity can be expected. The variation in the amount of water present as the saccharose becomes changed into dextrose and levulose must have some influence on the progress of the reaction, and one of the fundamental conditions of the Wilhelmy experiment is therefore not accurately observed. It has frequently been pointed out that the constant  $\frac{1}{t} \log. \frac{A}{A-x}$  may be quite irregular when calculated from tests on very strong solutions. The values are really constant only when the solvent is so greatly in excess that slight changes in it in the progress of the reaction, may be neglected. In the present case about two and five-tenths grams of water disappear in the formation of the new molecules, and this from a solution already very strong. Part of the irregularity in the constant may doubtless be explained in this manner. An accidental exposure to light during the last interval of the heating may partly account for the change in the last value.

It has been found by later experiments, some of which are still in progress, that with dilution of the solutions much more uniform results may be secured, approaching, in fact, those obtained from the action of weak acids alone.

The cause of the inversion of strong sugar solutions by these heavy salts is undoubtedly to be found in their condition of partial hydrolysis by the solvent. The acid ion in each case is a strong one, while the basic ions are all relatively weak. Indeed, it has been suggested by Walker and Aston<sup>1</sup> that the amount of hydrolysis in solutions of certain salts may be approximately measured by comparing the speed of inversion with that of known amounts of weak acids. The method can be easily applied to a large number of solutions of moderate concentration. Further investigations with special reference to ferrous salts are now in progress.

CHICAGO, DECEMBER, 1895.

## MIXED DOUBLE HALIDES OF PLATINUM AND POTASSIUM.

BY CHARLES H. HERTY.

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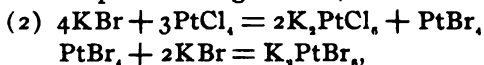
### INTRODUCTION.

BY mixing together water solutions of platinum chloride and potassium bromide in the proportion of one molecule of platinum chloride to two molecules of potassium bromide, Pitkin obtained<sup>2</sup> a compound having the composition represented by the formula  $K_2PtCl_4Br_2$ .

Two possible explanations were advanced by Pitkin,



a true chemical compound being formed, or



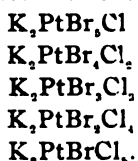
giving thus an isomorphous mixture of  $K_2PtCl_4$  and  $K_2PtBr_6$ . In either case the percentage of the elements remains the same. To determine which of the two explanations is correct, he resorted to fractional crystallization, and from the above solu-

<sup>1</sup> *J. Chem. Soc.*, July, 1895.

<sup>2</sup> *This Journal*, 1, 472.

tion obtained three successive crops of crystals. Determinations of platinum in each of these showed that they were identical, and he concludes, therefore, that the substance is a chemical compound and not an isomorphous mixture.

In a second paper<sup>1</sup> he described the series



These were prepared by mixing together stated quantities of  $K_2PtCl_6$  and  $K_2PtBr_6$ , dissolving in water and crystallizing. Three successive crops of  $K_2PtCl_6Br$  were obtained, showing respectively 36.97, 37.04 and 36.99 per cent. of platinum, again confirming the idea that these substances were true chemical compounds,

In the discussion, which followed the reading of the paper, Dr. Endemann suggested that these substances were most probably isomorphous mixtures.

In a third paper<sup>2</sup> Pitkin discussed the question of isomorphism and fractional crystallization, upholding his formerly expressed view that the platinum compounds were true chemical compounds. His argument was:

1. In isomorphism "the resulting mixed crystal has a composition dependent on the ratio, one to the other, of the isomorphous salts in solution or the constituents forming these salts."
2. "When two isomorphous salts together in solution are subjected to fractional crystallization, the salts differing in their degree of solubility in the menstruum employed, the crystals first formed will contain relatively a greater amount of the more insoluble salt, while the crystals formed at the end will be correspondingly rich in the more soluble salt."

It is principally upon the second consideration that he bases his claim that the substances are true chemical compounds and not isomorphous mixtures. This claim has been generally accepted and we find in many text books descriptions of the salt  $PtCl_6 \cdot 2KBr$ .

<sup>1</sup> This Journal, 2, 206.

<sup>2</sup> *Ibid.*, 2, 408.

Quite recently Pigeon<sup>1</sup> has prepared a substance to which he gives the formula  $K_2PtCl_2Br_2$ . He considers it one of the series previously prepared by Pitkin.

During the past few years I have been constantly occupied with efforts to prepare double halides containing more than one halogen. I have shown<sup>2</sup> that the double halides of lead and potassium and of antimony and potassium containing more than one halogen are isomorphous mixtures of the double halides containing one halogen. It has seemed desirable, therefore, to repeat the work of Pitkin and determine whether the facts upon which he based his reasoning are correct.

I may state in advance that his analytical results are altogether inaccurate and inadequate. The reasoning which he makes use of to prove that the substances are true chemical compounds, proves beyond doubt, when interpreted by the results which I have obtained, that the substances are isomorphous mixtures.

#### METHOD OF ANALYSIS.

In the analyses of his compounds Pitkin determined platinum alone. These determinations were made by heating the substance with oxalic acid, thoroughly washing the residue and weighing the dried spongy platinum.

Deeming the determination of platinum alone insufficient, I have analyzed all the compounds prepared during this investigation by reduction in hydrogen.

The hydrogen, generated in a Kipp apparatus, was purified by being passed through an acid solution of potassium permanganate, over moist copper carbonate, through alkaline permanganate solution, through water, and finally over calcium chloride, in the order named. The gas was then passed through a combustion tube, about twelve inches in length, in which was placed a porcelain boat containing a weighed quantity of the substance to be analyzed. The combustion tube, constricted at the end, was closely connected with a U tube in turn connected with another U tube, both tubes containing potassium hydroxide solution. Before analysis the dried crystals were finely powdered and thoroughly dried at  $110^\circ$ . After placing in the combustion

<sup>1</sup> Ann. Chem. Phys. [5] 2, 433.

<sup>2</sup> Ann. Chem. Phys. [5] 21, 31, and 16, 400.



tube the boat containing the substance to be analyzed, all air was driven out by the current of hydrogen. Gentle heat was then applied by means of a Bunsen burner with a winged top attachment. As the reduction proceeded the heating was slowly increased until the [flame from the burner almost touched the tube. This was maintained for some time. Finally the flame was removed and the tube allowed to cool, hydrogen passing through for one hour longer in order to remove all traces of hydrochloric or hydrobromic acids. The liquid in the U tubes was then transferred, with thorough rinsing, into a beaker and dilute nitric acid added in excess. The boat containing the metallic platinum and the potassium salts was removed from the tube and the mass thoroughly extracted with water by standing twenty-four hours. The platinum was then filtered in a porcelain Gooch crucible and thoroughly washed with water.

The crucible was then dried for one hour in an air-bath at  $110^{\circ}$ , heated to redness in a platinum crucible, allowed to cool, and weighed, the platinum being in the form of gray metal. In the filtrate from the platinum and in the neutralized liquid from the U tubes bromine and chlorine were determined by addition of an excess of standard solution of silver nitrate, filtering the precipitated silver halides in porcelain Gooch crucibles, and titrating the excess of silver in the filtrates with a standard solution of ammonium thiocyanate. The crucibles containing the silver salts were dried for three hours at  $150^{\circ}$ . From the weight of silver used and the weight of silver halides in the Gooch crucibles the weights of bromine and chlorine were calculated. In several cases the neutralized liquid from the U tubes was added to the filtrate from the platinum, the total bromine and chlorine being determined at one time.

In one salt potassium was determined as potassium sulphate by first removing the platinum by electrolysis, then evaporating with sulphuric acid in a weighed platinum dish.

In all of the analytical work vessels were allowed to stay on the balances ten minutes before being weighed. The atomic weights used were: platinum 194.34, potassium 39.03, chlorine 35.37, and bromine 79.76.

The above method of analysis is open to several criticisms.

In the first place the sodium nitrate in the neutralized liquid from the U tubes dissolves a small portion of the precipitated silver salts. In the second place, it is very difficult to remove all of the hydrochloric or hydrobromic acids from the finely divided platinum either by heating or by extraction with water.

In spite of these errors this method would seem to yield much more reliable results than the method of heating with oxalic acid, applicable for determinations of platinum alone.

#### PREPARATION OF MATERIALS.

The potassium bromide used in this investigation was heated sufficiently high to decompose any potassium bromate present and to drive off any ammonium chloride, repeatedly recrystallized from water, dried, finely powdered, and again thoroughly dried. Potassium chloride was prepared in the same manner.

Great difficulty was experienced in the preparation of pure chloroplatinic acid. This was unexpected, as previous investigators make no mention of any great difficulty. The purest specimens sent out by the manufacturers showed, on reduction in hydrogen, a coating of ammonium chloride on the combustion tube after raising the heat considerably. The substance was then prepared by dissolving platinum in aqua regia and evaporating repeatedly with hydrochloric acid. Still ammonium chloride was found after reduction with hydrogen. The constant appearance of ammonium chloride led to the hypothesis that some nitrogen compound might be present in the hydrogen used, and on coming into contact with the platinum black, in the presence of hydrogen and hydrochloric acid, might be converted into ammonium chloride. To test this point hydrogen was prepared from strictly pure zinc and the purest sulphuric acid which could be obtained. This hydrogen was then purified by Phillips' method.<sup>1</sup> Still ammonium chloride appeared after reduction of the platinum compounds.

The next explanation which suggested itself was the presence of some trace of the compound  $2\text{NOCl} \cdot \text{PtCl}_4$ , formed during the treatment with aqua regia. To eliminate this possible source of error, chloroplatinic acid was prepared by the method recommended by Pigeon,<sup>2</sup> in which no nitric acid is used. This

<sup>1</sup> *Am. Chem. J.*, 18, 195.

<sup>2</sup> *Ann. chim. phys.* [3], 2, 403.

method consists in precipitating the platinum as ammonium platinichloride, reducing this at a low temperature in hydrogen, and treating the finely divided platinum with hydrochloric acid and chlorine in a large flask, the chlorine being replenished as rapidly as it is taken up by the platinum.

A specimen prepared in this way also yielded ammonium chloride. While repeating this method of preparation an accident showed its unfitness for the purpose. According to directions a portion of the ammonium platinichloride had been reduced in hydrogen at a temperature just sufficient for the reduction, and the ammonium chloride evolved driven from the tube. Accidentally the temperature was considerably raised. Immediately quite a large deposit of ammonium chloride was formed on the combustion tube, showing that platinum black occludes ammonium chloride in quite large quantity. Efforts were made to remove all of the occluded ammonium chloride by prolonged heating in hydrogen but this proved very unsatisfactory. This method of Pigeon's is therefore unfit for use and there is little doubt but that the substances with which he conducted his thermochemical experiments were largely contaminated by ammonium platinichloride. A second method of Pigeon's was then tried. This consists in passing a current of chlorine gas through an emulsion of ammonium platinichloride and hot water. Nitrogen is given off and chloroplatinic acid formed, but on reduction in hydrogen ammonium chloride was again deposited. Finally, at the suggestion of Dr. H. N. Morse, of Johns Hopkins University, ammonium platinichloride was intimately mixed with pure oxalic acid and the mass heated to redness. A residue of spongy platinum was obtained which gave only a slight deposit of ammonium chloride on being heated in hydrogen. The platinum thus prepared was converted into chloroplatinic acid by treatment with chlorine and hydrochloric acid. The hydrochloric acid was prepared by heating concentrated chemically pure hydrochloric acid and passing the liberated gas into freshly distilled water. The chloroplatinic acid thus prepared still yielded a slight deposit of ammonium chloride.

Further attempts were made to purify this by cooling the solution, in the hope that the ammonium platinichloride would sepa-

rate from the solution, but this failed. Finally a current of chlorine gas was passed through a portion of this chloroplatinic acid solution for some time. The product still yielded a slight quantity of ammonium chloride on reduction in hydrogen. However, it was considered sufficiently pure for the purposes of the investigation and accordingly was used. All of the above processes were carried out in a room as free from ammonium chloride as was practicable.

The amount of platinum in the water solution of the chloroplatinic acid was determined by electrolysis.

One cc. solution = 0.08956 gram of platinum.

The use of chloroplatinic acid for determining potassium suggests that in addition to the precautions, already taken by the Association of Official Agricultural Chemists, of working in a room other than the general laboratory, more care should be taken in regard to the absence of ammonium platinichloride from the chloroplatinic acid as first sent out by the manufacturers.

#### METHOD OF WORK.

If the substances obtained by Pitkin are true chemical compounds it seems only natural to suppose that they could be reproduced under at least some slight variation in the original proportions of the substances used in their preparation. To determine this point four solutions were prepared, using the same amount of platinum solution in each. In one a definite quantity of potassium bromide was used. In the other three arbitrarily taken portions of the potassium bromide were replaced by equivalent quantities of potassium chloride. To prepare  $K_2PtCl_6Br_2$ , Pitkin used two grams platinum chloride and 1.404 grams of potassium bromide. These are the quantities required by using the atomic weights: platinum 197.18, chlorine 35.46, bromine 79.95, and potassium 39.13. More recent determinations of the atomic weight of platinum give the figure 194.34. The above quantities therefore evidently do not give the proportion  $PtCl_6:2KBr$ . However I have endeavored to meet this point by using 1.404 grams of potassium bromide and 12.00 cc of the platinum solution = 1.163 grams of platinum, conforming thus to the proportion  $PtCl_6:2KBr$  according to the atomic weights used by Pitkin.

In the replacement of potassium bromide by potassium chloride the more recent atomic weights were used. Potassium 39.03, chlorine 35.37, and bromine 79.76.

The quantities of the various substances actually used in the four experiments were :

TABLE I.

	H <sub>2</sub> PtCl <sub>6</sub> Sol. cc.	H <sub>2</sub> O. cc.	KBr. Grams.	KCl. Gram.
A .....	12.99	57.00	1.404	.....
B .....	12.99	57.00	1.200	0.1278
C .....	12.99	57.00	1.000	0.2531
D .....	12.99	57.00	0.800	0.3784

When the two solutions in each case were first mixed a small quantity of a light yellow precipitate was thrown down. On boiling with an inverted condenser all dissolved, the solutions becoming dark red. After cooling bright red octahedral crystals separated in each case, growing slightly lighter in color from A to D. The crystals were prepared for analysis as described above. On analysis the following results were obtained :

TABLE II.

	Pt. Per cent.	Cl in dis- tillate. Per cent.	Br in dis- tillate. Per cent.	Cl in resi- due. Per cent.	Br in resi- due. Per cent.	Total Cl. Per cent.	Total Br. Per cent.
A ..	34.93	23.19	4.47	4.74	18.12	27.93	22.59
B ..	35.90	24.91	2.03	6.19	15.47	31.10	17.50
C ..	36.46	26.02	1.04	7.58	12.93	33.60	13.97
D ..	37.07	26.73	0.31	8.41	11.44	35.14	11.75

TABLE III.

	Calculated for K <sub>2</sub> PtCl <sub>6</sub> Br <sub>2</sub> .	A.	B.	C.	D.	Calculated for K <sub>2</sub> PtCl <sub>6</sub> Br.
Pt per cent. ....	33.89	34.93	35.90	36.46	37.07	36.74
Cl " " .....	24.67	27.93	31.10	33.60	35.14	33.43
Br " " .....	27.82	22.59	17.50	13.97	11.75	15.08
Atomic ratio						
Pt : (Cl + Br) ....		1 : 5.97	1 : 5.95	1 : 6.00	1 : 5.98	....

From these results it is evident that four substances have been prepared, each differing in composition from the two nearest members of the series described by Pitkin, K<sub>2</sub>PtCl<sub>6</sub>Br, and K<sub>2</sub>PtCl<sub>6</sub>Br.

Furthermore the crystals show a variation in composition in

accord with the variation in composition of the solutions from which they formed. (See Table I). Yet in all four substances the atomic ratio of platinum to chlorine and bromine combined is practically 1:6. Again, if we assume C to be an isomorphous mixture of  $K_2PtCl_6$  and  $K_2PtBr_6$ , then 33.60 per cent. of chlorine requires 30.77 per cent. of platinum, while 13.97 per cent. of bromine requires 5.68 per cent. of platinum, giving the total per cent. of platinum required by this assumption 36.45. There was actually found 36.46 per cent.

In the hope of gaining some light upon the nature of these substances, separate determinations of chlorine and bromine were made in the portion which passed off in the current of hydrogen and in the portion combined with potassium in the residue. No definite conclusion on this point can be drawn from the results, except that a portion of the hydrobromic acid liberated decomposed a portion of the potassium chloride, setting free hydrochloric acid. Thermochemical considerations lead us to expect this as has been pointed out already by Pigeon. The results in Table III seem to show that the substances are isomorphous mixtures.

Pitkin's principal argument in support of the idea that the substances obtained by him were true chemical compounds is that the successive crops of crystals obtained from a solution of platinum chloride and potassium bromide are identical. Three successive crops were analyzed by him and gave the per cents. of platinum respectively, 34.22, 34.70, and 34.39. No determination of bromine or chlorine was made. To test this point more thoroughly the mother liquors from A, B, C, and D above were evaporated to about one-half of the previous volume and allowed to crystallize. Crystals were obtained in each case closely resembling the first crops obtained from the respective solutions. These crystals, designated A', B', C', and D', gave on analysis:

TABLE IV.

	Pt. per cent.	Cl. per cent.	Br. per cent.	Atomic ratio. Pt : (Cl+Br).
A'.....	33.48	25.37	26.26	1 : 6.08
B'.....	34.10	26.14	25.58	1 : 6.04
C'.....	35.27	28.30	22.25	1 : 5.95
D'.....	36.10	31.63	17.09	1 : 5.97

Potassium was determined in A'. There was found 13.59 per cent.

Finally the mother liquors from A', B', C' and D' were allowed to evaporate spontaneously until all water had passed off. A third crop of crystals was thus obtained in each case. These crystals closely resembled the former crops in regard to crystal form, but were much darker in color. They were designated A'', B'', C'' and D''.

A slight odor of hydrochloric or hydrobromic acid was noticed in each vessel when the evaporation was complete. On analysis the substances gave the following :

TABLE V.

	Pt. per cent.	Cl. per cent.	Br. per cent.	Atomic ratio. Pt : (Cl + Br).
A''.....	32.76	20.53	33.14	I : 5.91
B''.....	32.88	22.30	31.36	I : 6.05
C''.....	34.35	26.44	24.21	I : 5.95
D''.....	35.09	28.01	22.20	I : 5.93

By combining Tables II, IV and V it will readily be seen that the successive crops of crystals obtained from a solution are by no means identical, thus :

TABLE VI.

	Pt. per cent.	Cl. per cent.	Br. per cent.
A.....	34.93	27.93	22.59
A'.....	33.48	25.37	26.26
A''.....	32.76	20.53	33.14
B.....	35.90	31.10	17.50
B'.....	34.10	26.14	25.58
B''.....	32.88	22.30	31.36
C.....	36.46	33.60	13.97
C'.....	35.27	28.30	22.25
C''.....	34.35	26.44	24.21
D.....	37.07	35.14	11.75
D'.....	36.10	31.63	17.09
D''.....	35.09	28.01	22.20

If these results be arranged according to the per cent. of platinum, it will be seen that twelve substances have been prepared, each varying from the calculated per cents. for  $K_2PtCl_4Br_2$  or  $K_2PtCl_4Br$ , yet approaching these more nearly than any of the

other members of the series prepared by Pitkin. In all of the twelve the atomic ratio of platinum to chlorine and bromine combined, allowing for error in the analytical work, is practically 1 : 6, which is required if the substances are isomorphous mixtures :

TABLE VII.

	Pt. per cent.	Cl. per cent.	Br. per cent.	Atomic ratio Pt : (Cl + Br).
A'' .....	32.76	29.53	33.14	1 : 5.91
B'' .....	32.88	22.30	31.36	1 : 6.05
A' .....	33.48	25.37	26.26	1 : 6.08
B' .....	34.10	26.14	25.58	1 : 6.04
C'' .....	34.35	26.44	24.21	1 : 5.95
A .....	34.93	27.93	22.59	1 : 5.97
D'' .....	35.09	28.01	22.20	1 : 5.93
C' .....	35.27	28.30	22.25	1 : 5.95
B .....	35.90	31.10	17.50	1 : 5.95
D' .....	36.10	31.63	17.09	1 : 5.97
C .....	36.46	33.60	13.97	1 : 6.00
D .....	37.07	35.14	11.75	1 : 5.98

In addition to these, five other compounds were prepared. In these platinum was determined by electrolysis.

The per cents. of platinum found in these were 35.05, 34.94, 34.43, 34.00, and 33.26.

Pitkin relied upon analytical data in which no attention was paid to a variation of one-half per cent. and in one case one per cent. in the amounts of platinum present in different substances. Such were considered identical. By an inspection of Table VII it will be seen that such a variation in the platinum means so great a variation in the chlorine and bromine that it is impossible to consider such substances identical.

From the above evidence there seems little doubt but that the substances are isomorphous mixtures. To test the point still further a large portion of A was dissolved in hot water; on cooling, crystals quite similar to A separated. These were dried and designated X. The analytical results are placed side by side with those of A for convenience in comparing the two.

TABLE VIII.

	Pt. per cent.	Cl. per cent.	Br. per cent.	Atomic ratio Pt : (Cl + Br).
A .....	34.93	27.93	22.59	1 : 5.97
X .....	35.48	26.36	18.50	1 : 5.93



By recrystallization the first crop obtained was thus evidently richer in the more insoluble compound,  $K_2PtCl_6$ . This would be expected in the case of an isomorphous mixture of two substances differing in their degree of solubility.

Further evidence of the mixed nature of the substances was obtained by placing a considerable quantity of the substance X in a well fitting glass stoppered bottle, pouring upon the finely powdered substance a quantity of water quite insufficient for complete solution in the cold, placing the stopper in the bottle and shaking thoroughly several days. After being shaken for a short time and the undissolved portion allowed to settle, it was found that instead of the homogeneous powder, originally present in the bottle, two distinct layers were now present, one a dark red, the other a light yellow. Evidently the water had dissolved the more soluble red bromide to a larger extent than the less soluble yellow chloride. After four days the liquid was filtered from the undissolved residue. This residue was thoroughly dried, powdered, and intimately mixed and labelled Y. Its analysis, compared with the original substance X showed

TABLE IX.

	Pt per cent.	Cl per cent.	Br per cent.	Atomic ratio. Pt : (Cl + Br).
X .....	35.48	29.96	18.80	1 : 5.93
Y .....	35.87	30.98	17.80	1 : 5.96

confirming thus the idea that the more soluble bromide had dissolved to a larger extent than the less soluble chloride.

## SUMMARY.

Four lines of evidence have thus been adduced, all pointing to the conclusion that the double halides of platinum and potassium containing more than one halogen are isomorphous mixtures of different double halides containing only one halogen :

1. The formation of a series of substances varying in composition approximately as the variation in the composition of the solutions from which they crystallized. None of these substances correspond to the formulas proposed by Pitkin, but all show an approximate atomic ratio, platinum to chlorine and bromine, of 1:6. Fifteen other substances, all varying in composition, have been prepared ; in ten of these the atomic ratio of platinum

to chlorine and bromine was found to be practically 1 : 6, in the other five platinum alone was determined.

2. The successive crops of crystals obtained from a water solution of chloroplatinic acid and potassium bromide are not identical, but show gradually increasing proportions of the more soluble potassium platinibromide and correspondingly decreasing proportions of the less soluble potassium platinichloride.

3. On recrystallizing from water one of the substances under examination, the first crop of crystals is not identical with the original substance but is a product richer in chlorine and correspondingly poorer in bromine. This is to be expected on recrystallizing an isomorphous mixture of two substances differing in degree of solubility.

4. On treating one of the substances obtained with a quantity of water insufficient for complete solution, the more soluble bromide was dissolved from the mass to a greater extent than the less soluble chloride. This was confirmed both by the appearance of the insoluble residue and its analysis.

At the beginning of this investigation Mr. Henry Hillyer, Jr., a student in this laboratory, was associated with me in the work. His sad death at his home in Augusta, Ga., on April 4, 1895, terminated this association. I desire to here pay tribute to his rare qualifications as an investigator and to the manliness which characterized his every act.

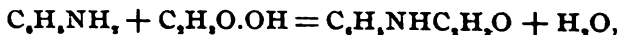
UNIVERSITY OF GEORGIA,  
NOVEMBER 9th, 1895.

## THE QUALITATIVE EXAMINATION OF ACETANILID.

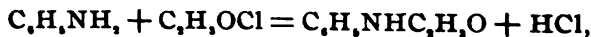
BY CHARLES PLATT.

Received November 22, 1895.

IN view of the deficiency in the analytical literature of the acid anilids the following tests may prove of interest. The formation of acetanilid, or phenylacetamid,  $C_6H_5NHC_2H_5O$ , from anilin and glacial acetic acid



and the corresponding formation from anilin and acetyl chloride



suggest the adaptability of various color reactions with the acids and alkalies. The physical constants have been determined and the decomposition of the anilid made to serve for its identification.

Acetanilid is a white crystalline powder neutral in reaction and tasteless but producing a slight burning sensation when placed upon the tongue. Examined under the microscope it is found to be made up of broken crystalline plates. The melting point, commonly given as  $113^{\circ}$ – $114^{\circ}$ , is determined by the writer as fairly constant at  $112^{\circ}$ . Heated on platinum, acetanilid volatilizes without leaving a residue, and, when ignited, it burns completely with a yellow flame. At  $15^{\circ}$  it is soluble in about 190 parts of water and in five parts of alcohol. It is soluble in eighteen parts of boiling water and in about five-tenths part of boiling alcohol. It is soluble in the cold in ether, chloroform, acetic acid, nitric and sulphuric acids, and, when warmed, in hydrochloric acid. On boiling with water, oil-like globules separate out and the solution on cooling recrystallizes in large but delicate six-sided plates.

*Reaction with Concentrated Nitric Acid.*—Acetanilid is easily soluble in strong nitric acid, the solution being colorless in the cold but turning to a yellow, then brownish red, on gentle warming, nitrogen oxides being at the same time evolved. The colorless solution on standing in the cold gradually acquires a light green tint but finally changes, through yellow, to red, with formation of red acicular crystals. This red solution gives off the odor of nitrobenzene. A similar appearance and odor are produced by evaporating nitric acid solutions; an oily residue of decided odor being produced by rapid evaporation, a crystalline residue of slight odor by slow evaporation. The nitric acid solution has been described by one writer as colorless; by another as brown, then blue, then colorless.

*Reaction with Dilute Nitric Acid.*—The acetanilid is slowly soluble in the cold, and without change in color but with separation of oil-like globules. This solution on slow evaporation gives a brown residue with slight purplish tint. By boiling with dilute nitric acid a colorless solution is obtained, with evolution of pungent fumes.

*Reaction with Concentrated Sulphuric Acid.*—A colorless solution is formed, unaffected by heating to boiling. The solution in cold concentrated acid, on long standing, acquires a pink to brown color. With an excess of the acetanilid the pink coloration develops quickly, is well marked, and changes gradually to an orange by reflected light. As a final change tufts of delicate acicular crystals appear and the solution gradually becomes colorless.

*Reaction with Sulphuric Acid and Potassium Chromate.*—A solution in concentrated sulphuric acid is turned to a dark green on addition of a few drops of potassium chromate. A solution in concentrated sulphuric acid, subsequently diluted, gives no reaction at first with the potassium chromate but on standing is gradually turned to a reddish-brown, and finally to a dark olive-green. A similar reaction to the last is produced by addition of the chromate to a solution in cold dilute acid.

*Reaction with Hydrochloric Acid.*—The acetanilid easily dissolves in hydrochloric acid when warmed and no precipitate is produced by subsequent dilution with water.

With hydrochloric acid and potassium dichromate there is no well marked reaction.

*Reaction with Hydrochloric Acid and Potassium Permanganate.*—An olive-green coloration is obtained by adding a small crystal of the potassium permanganate to the solution in hydrochloric acid. On standing the color is changed to a mahogany-brown.

*Reaction with Hydrochloric Acid and Chromic Acid.*—A solution of acetanilid in hydrochloric acid, diluted, and treated with a weak solution of chromic acid gives a yellowish-green coloration, which gradually turns to a dark green. Potassium hydroxide produces a blue precipitate in this solution.

*Reaction with Hydrochloric Acid and Bromine.*—Bromine water added in excess to a solution in hydrochloric acid produces a heavy yellow to white precipitate of the monobrom derivative of anilin. This precipitate examined microscopically is found to be made up of a fine interlacing net-work of needles or fiber-like crystals. A similar precipitate is obtained by means of bromine water in a water solution of the acetanilid.

*Reaction with Hydrochloric Acid and Chlorine.*—Chlorine water

added to a solution in hydrochloric acid gives a dark blue coloration which afterwards fades. A similar reaction is obtained by substituting for the chlorine water a filtered solution of bleaching powder.

Mercuric chloride added to the hydrochloric acid solution gives no precipitate.

Dissolve some of the powder in a little hydrochloric acid and add, first, a few cc. of five per cent. phenol, then a little clear saturated solution of chlorinated soda or lime. The solution acquires a brownish-red color turning to a blue on addition of ammonium hydroxide in excess.

*Reaction with Potassium Hydroxide.*—By heating some of the powder with potassium or sodium hydroxide the characteristic odor of anilin is developed.

*Reaction with Potassium Hydroxide and Chloroform.*—By heating with potassium or sodium hydroxide and a few drops of chloroform the characteristic odor of an isonitrile is developed, phenylisocyanide being formed.

*Reaction with Sodium Nitrite and Sulphuric Acid.*—The powder mixed with sodium nitrate and sprinkled upon concentrated sulphuric acid produces a fine red coloration.

*Reaction with Ferric Chloride.*—A cold saturated water solution added to neutral ferric chloride produces no change in color.

*Reaction with Zinc Chloride.*—Acetanilid heated to  $270^{\circ}$  with an equal weight of zinc chloride produces, first, orthoamidoacetophenone, in small amount, and then flavanilin  $C_6H_5N$ , a yellow substance with a green fluorescence, a derivative of quinolin. It is stated in a number of text-books that acetanilid boiled with zinc chloride, anilin, and acetic acid will produce amidoacetophenone,  $C_6H_5NH.C_6H_5O$ , but this test is untrustworthy inasmuch as the reagents used will produce this substance in absence of acetanilid. The paramidoacetophenone produced is crystalline in nature, while the ortho derivative formed in the previous test by heating zinc chloride and acetanilid is a yellow oil of high boiling point and with a characteristic sweetish odor.

*Reaction with Plugge's Reagent.*—Boil the acetanilid with water, cool and filter off if necessary, then boil again with potas-

sium nitrite and dilute nitric acid. Mix with Plugge's reagent, a solution of mercurous nitrate with a little nitrous acid, and again heat to boiling. A deep red color is developed.

Antipyrin and phenacetin, two other popular antipyretics much used in medicine, may be readily distinguished from acetanilid by the foregoing tests. Antipyrin, for instance, with ferric chloride gives a deep-red coloration and is precipitated from its solutions by mercuric chloride. It has approximately the same melting point as acetanilid, but, unlike the latter, is decomposed by further heating. The characteristic reactions for phenacetin have been given by the writer in a former article.<sup>1</sup>

Comparative tests have been made upon various samples of acetanilid of domestic and foreign manufacture. The products of reputable houses seem to be practically identical with the exception of difference in perfection of crystallization and a corresponding difference in appearance.

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## HEATS OF SOLUTION OF SOME CARBON COMPOUNDS.

BY C. L. SPEYERS.

Received October 14, 1895.

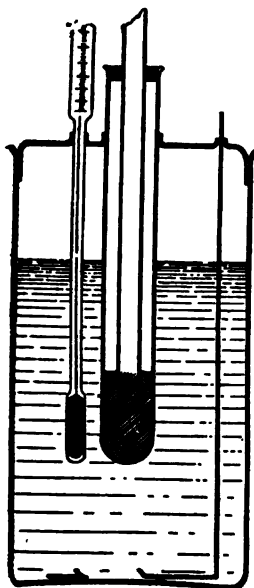
THE following paper contains a few data about the heats of solution of some solid carbon compounds in water, methyl alcohol, ethyl alcohol, propyl alcohol, chloroform, and toluene.

The simple method given by Nernst<sup>2</sup> was used.

The calorimeter was made of thin glass. The rim was ground to take the cover which fitted fairly well against the inside ground rim of the beaker, not air tight but tight enough to prevent appreciable evaporation of the more volatile solvents during the experiment. The cover had three holes with short tubulures. The center tubulure carried a test tube firmly fastened with a cork, the second tubulure as close to the center one as possible, carried the thermometer, while the third one, somewhat farther from the center, let the handle of the platinum stirrer pass through; see figure. The calorimeter held com-

<sup>1</sup>*J. Anal. Appl. Chem.*, 7, 2.

<sup>2</sup>*Ztschr. phys. Chem.*, 2, 23.



fortably 375 cc., none of the liquid spattering against the cover while stirring. In calculating the water value of the calorimeter, the cover, being some distance from the surface of the solution, was not considered; as the calorimeter without the cover weighed 64.70 grams, its value was  $64.70 \times 0.195 = 12.63$  grams. Later on this calorimeter was broken and replaced by another whose value was  $69.44 \times 0.195 = 13.54$  grams water. The first calorimeter with cover weighed 87.60 grams, the second one, 94.90 grams.

The bottom of the test tube which held the substance to be dissolved was about two inches below the surface of the solvent. A glass tube closed at both ends and blown out a little at one end, projected above the protecting vessels of the calorimeter and ran down to the bottom of the test tube. A sharp tap on the top shattered the bottom of the test tube and the solvent entering quickly dissolved the solid when the latter was rubbed off the sides of the test tube by the swelled tube. This was quite necessary, for the finely powdered solids made a pasty mass with the solvent and stuck tenaciously to the test tube.

The test tubes were so near the same size and dipped so equally into the solvent that the water value of this part could be considered constant. In a few exceptional cases the test tubes were of a different size. The same plunger was used throughout.

The platinum stirrer was made of ordinary laboratory foil stiffened with wire. It was disk-shaped and about nine cm. in diameter. From the circumference inward, about one cm., and then parallel with the circumference about two cm., cuts were made. The pieces thus partly cut loose were bent alternately up and down. A stout platinum wire was welded to the

disk, and ended in a cork, to serve as a non-conducting handle. A circular hole in the center let the thermometer and test tube pass through. This stirrer has already been described in the chemical literature;<sup>1</sup> it was very effective. Its total weight, without cork, was 12.036 grams, but as only 9.948 grams dipped into the liquid, its value was taken to be  $9.948 \times 0.0324 = 0.322$  grams of water.

The thermometer was made by Götze some seven years ago. It was divided into hundredths of a degree and thousandths could easily be estimated when observing through a telescope. Its value was determined by cooling in ice and plunging into the calorimeter, as well as by measurement and computation; it was 1.0 gram water. It was carefully calibrated.

The solutions were so dilute, their specific heats could be reasonably considered equal to those of the pure solvents.

The calorimeter stood on three hard wood pins in a bright tin vessel, large enough to leave an air space of an inch all around. The sides and top of the tin vessel were covered with felt. This tin vessel in turn stood on three pins in another bright tin vessel, leaving an air space of two inches all around. The sides and top of this tin vessel were likewise covered with felt. In turn, it stood in a third bright tin vessel, leaving an air space of two inches all around. This last vessel had only a top cover of felt. It was immersed to within an inch of the top in water contained in a large galvanized tank about seventy-five cm. in diameter and thirty cm. deep. The temperature of the water was kept around 25°.

These arrangements were required because the experiments were carried on at night in a small room and the abundant radiation had to be checked. They answered the purpose.

The solvent was contained in a calibrated flask. This stood on a piece of felt in a bright tin vessel, whose sides and top were covered with felt. This vessel in turn stood on three hard wood pins in another bright tin vessel, which had only a top cover of felt because it was immersed to within an inch of the top in the water of the large tank just mentioned. The flask was carefully calibrated for delivery. It had a long neck with a felt wrapping

<sup>1</sup> I cannot recall where



to protect against the heat of the hand when pouring out the solvent.

Some hours before an experiment was to be made the flask was filled and put in the proper vessel in the tank. The calorimeter, with substance in the test tube, and test tube, thermometer, and stirrer, in place, was also put in the proper vessel in the tank. When the time came, the solvent was carefully poured into the calorimeter and the apparatus put together again. The mercury in the thermometer soon assumed a slow, regular motion. Observations were then made every minute for five minutes, at the same time the liquid was stirred slowly and regularly. At the end of the fifth minute a sharp tap on the projecting glass tube shattered the bottom of the test tube and a few up and down rubs removed the pasty mass from the walls of the tube. The stirring was kept up all the time, slowly and regularly. The solution was generally completed within a minute, but in any case, no more than five minutes were required for complete solution. The mercury then resumed the previous slow and regular movement. The beginning of this regular movement was sharply marked and showed when solution was complete. The mercury was again observed every minute for another five minutes. The change in temperature from the time of adding the solid to the time of slow and regular movement was considered as the change in temperature produced by dissolving the substance.

The corrections were calculated by Regnault's and Pfaundler's method.<sup>1</sup>

In the following tables, these abbreviations are used :

$m$  = mass of substance dissolved in grams.

$\Delta t_1$  = Average change in temperature for one minute during the first five minutes.

$\Delta t_2$  = ditto during the second five minutes.

$t$  = correction.

$\Delta T$  = corrected change in temperature produced by dissolving the substance.

$M$  = value in grams of water, of liquid, calorimeter, thermometer, test tube, and plunger.

<sup>1</sup> See Berthelot : *Calorimétrie chimique*, p. 47.

$q$  = quantity of heat in small calories connected with the solution of  $m$  grams of substance.

$Q$  = quantity of heat in small calories connected with the solution of one gram molecule of substance.

$T$  = temperature of solvent at commencement of experiment.

#### HEATS OF SOLUTION IN WATER.

The water was carefully distilled, but was not further purified.

##### *Urea.*

The urea came from Merck; it was recrystallized from alcohol, powdered, and dried. Melting point =  $132.7^{\circ}$  cor.; melting point according to Beilstein =  $132^{\circ}$ .

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
3.2909	+0.0008	-0.0018	-0.004	-0.518	389.4	-201.7	-3690	24.5 <sup>c</sup>
1.1498	-0.0014	-0.0014	-0.001	-0.176	389.6	-68.57	-3577	24.2 <sup>c</sup>

Average, -3628.5 cal.

Thomsen gives 3349 calories; Ostwald, quoting Berthelot and Petit, gives 36 K, where K may be considered as 100 calories.

##### *Urethane.*

The urethane came from Kahlbaum. Melting point =  $48.5^{\circ}$  cor. It was melted, dried, and powdered. Melting point =  $47.33^{\circ}$  cor. Tested for chlorine, but none found.

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
4.3687	-0.0026	-0.0048	-0.005	-0.479	388.4	-186.6	-3801	22.5 <sup>c</sup>
0.9380	-0.0026	-0.0020	-0.002	-0.102	389.8	-39.74	-3773	23.5 <sup>c</sup>

Average, -3787 cal.

##### *Chloral Hydrate.*

From Kahlbaum. Aqueous solution slightly acid. On adding silver nitrate and nitric acid to an aqueous solution a slight precipitate formed after twenty-four hours. Concentrated sulphuric acid caused the separation of chloral, without any coloration. Melting point =  $49.4^{\circ}$  cor. Beilstein quotes melting point =  $57^{\circ}$ ; Fehling gives figures varying from  $46^{\circ}$  to  $58^{\circ}$ .

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
10.6187	-0.0010	-0.0018	-0.002	-0.175	389.8	-68.20	-1061	23.5 <sup>c</sup>
3.7933	-0.0024	-0.0028	-0.004	-0.047	389.6	-18.31	-797	22 <sup>c</sup>

Average, -929 cal.

Ostwald quoting Berthelot would make the heat of solution 8.1 K on 810 cal. at 22°, the heat of solution decreasing with rising temperature.

*Succinimide.*

From Kahlbaum. Recrystallized from water and dried at 85°-100°. Small quantity of white fume given off at about 95°. Melting point = 124.5° cor. Beilstein gives 125°-126°.

M.	$\Delta t_1$	$\Delta t_2$	t.	$\Delta T$	M.	q.	Q.	T.
5.5606	-0.0040	-0.0080	-0.024	-0.621	389.6	-242.0	-4306	21.5°
2.3592	-0.0026	-0.0024	-0.002	-0.262	389.5	-102.0	-4282	23.2°
							Average,	-4294 cal.

*Acetamide.*

From Eimer and Amend. Distilled in ammonia and stirred while cooling to get small crystals. Seemed to be slightly moist though carefully protected from the air. Melting point =  $73.3^{\circ}$  cor. Beilstein gives  $82^{\circ}$ – $83^{\circ}$ . Fehling gives  $78^{\circ}$ .

m.	$\Delta t_1$	$\Delta t_2$	t.	$\Delta T$	M.	q.	Q.	T.
5.1249	0.0000	-0.0006	-0.001	-0.439	389.6	-171.0	-1969	24.0°
2.7516	-0.0016	-0.0022	-0.002	-0.241	389.7	-93.90	-2014	23.0°
					Average, —1991 cal.			

Ostwald, quoting Berthelot and André, gives 19 K or 1900 cal.

**Mannite.**

From Kahlbaum. Crystalline white. Was not further purified. Melting point =  $165.5^{\circ}$  cor. Beilstein gives  $164^{\circ}$ – $166^{\circ}$ .

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
4.5287	-0.0028	-0.0056	-0.011	-0.335	389.5	-130.5	-5245	22.5 <sup>c</sup>
2.1767	-0.0004	-0.0010	-0.001	-0.162	389.8	-63.14	-5279	23.5 <sup>o</sup>
							Average,	-5262 cala.

*Sugar.*

Prepared from the purest rock candy obtainable. Only well developed crystals were kept. These were washed with water, dried, and powdered. Only a trace of glucose could be found.

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
6.3794	-0.0006	-0.0004	-0.001	-0.061	389.8	-23.73	-1275	23.0°
2.6436	+0.0004	+0.0002	-0.000	-0.027	189.4	-10.52	-1361	22.7°
					Average,		-1318 cal.	

*Resorcinol.*

From Kahlbaum. Crystallized. Was assumed to be pure. Melting point =  $110.6^{\circ}$  cor. Decomposed a little on melting. Beilstein gives melting point =  $110^{\circ}$  and  $119^{\circ}$ .

m.	$\Delta t_1$	$\Delta t_2$	t.	$\Delta T$	M.	q.	Q.	T.
6.0850	-0.0020	-0.0030	-0.003	-0.564	389.6	-219.7	-3970	$23.5^{\circ}$
3.0595	+0.0040	-0.00060	-0.001	-0.282	389.6	-109.8	-3950	$22.5^{\circ}$

Average,  $-3960$  cal.

## HEATS OF SOLUTION IN METHYL ALCOHOL.

Methyl alcohol from Kahlbaum. Labeled "Acetonfrei." Dehydrated with large excess of calcium oxide. After twenty-four hours distilled. Portion coming over at  $64.3^{\circ}$  cor was used. Sp. gr.  $\frac{15^{\circ}}{4} = 0.79619 = 99.9$  per cent. methyl alcohol by Landolt's and Bjornstein's tables. Mass of alcohol delivered between  $20^{\circ}$ - $25^{\circ} = 373.9 \times 0.7870 = 294.3$  grams, or in water terms =  $294.3 \times 0.62 = 182.4$  grams water.

*Urethane.*

m.	$\Delta t_1$	$\Delta t_2$	t.	$\Delta T$	M.	q.	Q.	T.
1.5032	-0.0032	-0.0068	-0.014	-0.369	198.8	-73.36	-4346	$24^{\circ}$

*Acetanilid.*

From Kahlbaum. Recrystallized from alcohol. Air dried. White. Slight, agreeable, aromatic odor. Melting point =  $113.5^{\circ}$  cor. Beilstein gives  $112^{\circ}$ ; Fehling gives from  $101^{\circ}$ - $113^{\circ}$ .

m.	$\Delta t_1$	$\Delta t_2$	t.	$\Delta T$	M.	q.	Q.	T.
2.1823	-0.0020	-0.0072	-0.018	-0.361	198.8	-72.38	-4477	$24.5^{\circ}$

*Acenaphthene.*

From Kahlbaum. White. Recrystallized from alcohol. Air dried. Melting point =  $93.5^{\circ}$  cor. Beilstein gives  $95^{\circ}$  and  $101^{\circ}$ ; Fehling gives over  $100^{\circ}$ .

m.	$\Delta t_1$	$\Delta t_2$	t.	$\Delta T$	M.	q.	Q.	T.
1.4266	-0.0072	-0.0082	-0.008	-0.288	198.8	-57.26	-6180	$24^{\circ}$

*Naphthalene.*

From Kahlbaum. White. Recrystallized from alcohol. Air dried. Melting point =  $80.1^{\circ}$  cor. Beilstein gives  $79.2^{\circ}$  and  $80.1^{\circ}$ .

m.	$\Delta t_1$	$\Delta t_2$	t.	$\Delta T$	M.	q.	Q.	T.
1.3381	-0.0018	-0.0038	-0.008	-0.220	198.8	-41.94	-4233	$24^{\circ}$

## HEATS OF SOLUTION IN ETHYL ALCOHOL.

Ethyl alcohol from Eimer and Amend and Chas. Cooper and Co. Marked absolute. Distilled, treated with calcium oxide, and redistilled. Boiling point,  $77.6^{\circ}$ – $78.7^{\circ}$  cor. Sp. gr. = 0.7873. Mass of alcohol delivered between  $20^{\circ}$  and  $25^{\circ}$  =  $373.9 \times 0.7873$  = 294.4 grams, or in water terms =  $294.4 \times 0.59$  = 173.7 grams water.

*Urethane.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
3.4826	–0.0010	–0.0084	–0.019	–0.976	190.3	–185.7	–4746	$23.5^{\circ}$
2.5207	–0.0110	–0.0172	–0.017	–0.701	190.3	–133.4	–4710	$23.8^{\circ}$
Average,							–4728 cal.	

*Acetanilid.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
2.8726	+0.0014	–0.0048	–0.009	–0.471	190.3	–89.74	–4212	$23^{\circ}$

*Acenaphthene.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
3.8306	+0.0038	–0.0046	–0.009	–0.772	190.1	–146.7	–5899	$25.0^{\circ}$
1.6855	–0.0014	–0.0024	–0.005	–0.340	190.3	–64.71	–5914	$23.6^{\circ}$
Average,							–5906 cal.	

*Naphthalene.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
2.9976	–0.0036	–0.0104	–0.021	–0.599	190.1	–113.9	–4861	$24^{\circ}$

*Urea.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
1.3715	+0.0003	–0.0046	–0.025	–0.434	190.1	–82.6	–3612	$24^{\circ}$

*Acetamide.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
3.4805	+0.0014	–0.0094	–0.019	–1.119	190.1	–212.7	–3606	$23.3^{\circ}$

*Phenanthrene.*

From Kahlbaum. Crystallized three times from toluene. Air dried. Melting point =  $100.4^{\circ}$ . Beilstein gives  $99^{\circ}$ ; Fehling gives  $96^{\circ}$  to  $100^{\circ}$ .

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
0.8259	–0.0008	–0.0022	–0.004	–0.105	190.3	–19.98	–4306	$24^{\circ}$

*Chloral Hydrate.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
3.0642	–0.0022	–0.0182	–0.018	–0.029	190.3	–5.519	–113.1	$22^{\circ}$

*Succinimide.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
4.1413	-0.0018	-0.0106	-0.032	-1.199	190.3	-228.2	-5456	21.5°

*Benzamide.*

From Kahlbaum. Recrystallized from water. Air dried, Melting point 126.0°. Beilstein gives 123°; Fehling gives 125°.

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
1.9457	-0.0018	-0.0052	-0.005	-0.361	190.3	-68.7	-4238	22.5°

*Resorcinol.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
4.2003	-0.0016	-0.0016	-0.0024	+0.054	190.3	+10.28	+2692	22.5°

*Toluidin (p).*

From Kahlbaum. Very impure. Recrystallized from alcohol three times. Slightly yellowish, turned darker on exposure to air and light while drying. Air dried. Melting point 44.6°. Beilstein gives 45°.

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
3.4900	-0.0018	-0.0074	-0.007	-0.623	190.3	-118.6	-3636	23.5°
1.3391	+0.0014	-0.0008	-0.001	-0.241	190.3	-45.87	-3665	24°

Average, -3650 cal.

## HEATS OF SOLUTION IN PROPYL ALCOHOL.

Propyl alcohol from Kahlbaum. Dehydrated with calcium oxide. Distilled. Distillate collected until an empyreumatic odor was observed. Sp. gr.  $\frac{24^\circ}{4^\circ} = 0.80128$ . Mass of alcohol delivered between 20° and 25° =  $373.9 \times 0.8013 = 299.5$  grams, or in water terms =  $299.5 \times 0.66 = 197.7$  grams water.

*Urethane.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
3.3360	-0.0144	-0.0212	-0.021	-1.054	214.3	-225.9	-6045	24.7°

*Acenaphthene.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
3.0744	-0.0152	-0.0198	-0.040	-0.634	214.3	135.9	-6807	13°

*Naphthalene.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
2.6408	-0.0112	-0.0158	-0.032	0.547	214.3	-117.2	-5681	23.0°

## HEATS OF SOLUTION IN CHLOROFORM.

Chloroform from Eimer and Amend, Powers and Weightman,

and Charles Cooper and Co. Purified by washing with water till it gave no reaction for alcohol, drying with sulphuric acid or calcium chloride and distilling. No reaction for impurities with silver nitrate or potassium hydroxide. Sp. gr. between  $20^{\circ}$  and  $25^{\circ} = 1.479$ . Mass of chloroform delivered  $= 373.9 \times 1.479 = 553.0$  grams, or in water terms  $= 553.0 \times 0.2337 = 129.3$  grams water.

*Urethane.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
3.2930	+0.0014	-0.0082	-0.032	-1.161	145.7	-169.2	-4573	23.5°

*Acetanilid.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
2.5859	+0.0026	-0.0038	-0.022	-0.584	145.7	-85.10	-4442	24.5°

*Acenaphthene.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
2.4138	+0.0008	-0.0072	-0.035	-0.482	145.7	-70.23	-4480	21°

*Naphthalene.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
0.9407	-0.0060	-0.0052	-0.005	-0.194	145.9	-28.31	-3852	23°

*Chloral Hydrate.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
7.0497	-0.0042	-0.0368	-0.137	-1.753	145.9	-255.7	-5993	21.7°

*Toluidin (p).*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
1.2787	-0.0028	-0.0034	-0.011	-0.286	145.9	-41.74	-3492	23.3°

## HEATS OF SOLUTION IN TOLUENE.

From Kahlbaum, Colorless. Redistilled. Boiling point  $110.4^{\circ}$ - $110.7^{\circ}$ . Sp. gr. between  $20^{\circ}$  and  $25^{\circ} = 0.8621$ . Mass of toluene delivered  $= 373.9 + 0.8621 = 322.3$  grams, or in water terms  $= 322.3 \times 0.3942 = 127.1$  grams water.

*Urethane.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
1.7615	-0.0002	-0.0100	-0.018	-0.881	143.7	-126.6	-6399	23°

*Acenaphthene.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
5.1897	-0.0066	-0.0202	-0.020	-1.115	143.9	-160.6	-4763	23°
1.6799	-0.0062	-0.0100	-0.010	-0.366	143.5	-52.51	-4814	23°

Average, -4788 cal.

*Naphthalene.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
2.3937	-0.0010	-0.0074	-0.007	-0.550	143.9	-79.13	-4232	23°
0.9916	-0.0034	-0.0064	-0.013	-0.232	143.7	-33.34	-4302	23°
Average,							-4267	cal.

*Chloral Hydrate.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
2.8739	-0.0090	-0.0156	-0.056	-0.913	143.5	-131.0	-7537	24°

*Phenanthrene.*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
3.6075	-0.0046	-0.0076	-0.015	-0.504	153.7	-72.71	-3588	24.7°
1.3179	-0.0084	-0.0108	-0.011	-0.179	143.5	-25.69	-3469	23°
Average,							-3528	cal.

*Toluidin (p).*

m.	$\Delta t_1$ .	$\Delta t_2$ .	t.	$\Delta T$ .	M.	q.	Q.	T.
3.8683	-0.0080	-0.0186	-0.019	-1.247	143.7	-179.2	-4956	24.7°
1.9525	+0.0024	-0.0032	-0.003	-0.636	143.7	-91.40	-5011	23°
Average,							-4983	cal.

The quantity of solvent compared with the quantity of substances dissolved is so large that it is safe to conclude that further addition of solvent would produce no appreciable evolution of heat. Besides, it is plain from the above experiments that in many cases a difference of 100 per cent. in the quantity of solvent produced no decided change.

The following table shows the heats of solution in a convenient form for comparison.

	Water.	Methyl alcohol.	Ethyl alcohol.	Propyl alcohol.	Chloroform.	Toluene
Urea .....	-3628	.....	-3612	.....	.....	.....
Urethane .....	-3787	-4345	-4728	-6045	-4573	-6399
Chloral hydrate .....	-929	.....	-1131	.....	-5993	-7537
Succinimide ..	-4294	.....	-5456	.....	.....	.....
Acetamide ....	-1991	.....	-3606	.....	.....	.....
Mannite .....	-5262	.....	.....	.....	.....	.....
Resorcin .....	-3960	.....	+269.2	.....	.....	.....
Benzamide ....	.....	.....	-4238	.....	.....	.....
Toluidine (p) .....	.....	.....	-3650	.....	-3492	-4983
Acetanilide ..	.....	-4477	-4212	.....	-4442	.....
Acenaphthene ..	.....	-6180	-5986	-6807	-4480	-4788
Naphthalene ..	.....	-4233	-4861	-5681	-3852	-4267
Phenanthrene ..	.....	.....	-4306	.....	.....	-3528
Sugar .....	-1318	.....	.....	.....	.....	.....



## A STUDY OF SOME GAS-PRODUCING BACTERIA.

BY A. A. BENNETT AND E. E. PAMMEL.

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THE manifold interests connected with micro-organisms, because of their causal relations to certain diseases of man and also of the lower animals, and the part they play in many important economic problems have stimulated much investigation by physicians and biologists. The field is, however, very great and the explorations have but just begun.

There are many questions connected with this subject that are yet unsettled and many that have not as yet been touched upon. The physician in studying micro-organisms has always before him the consideration of their relation to the disease in question. Other phases of the life of these germs are not at all considered by these investigators, thus leaving the important questions of classification, physiology and the chemistry of their life and development to the botanist and chemist. The purpose of this paper is to make a small contribution to a phase of the chemical side of this question, namely, to a study of the gases produced during the development and growth of some micro-organisms.

Although the study of the products of chemical decomposition formed by micro-organisms has not been very extensive or very thorough, yet much has been learned in a qualitative way. The substances produced by bacteria are quite numerous, including solids, liquids and gases. The same products are often produced by different organisms in varying proportions.

Among the solids produced are the ptomaines, indol, skatol, leucine, tryrosine, succinic and malic acids, etc. The liquid products include alcohol, acetic and lactic acids. The gases formed are quite numerous and include hydrogen sulphide, ammonia, carbon dioxide, hydrogen and methane. In cases in which ammonia and hydrogen sulphide are produced simultaneously, they unite and form ammonium sulphide.

The importance of the study of these compounds, both qualitatively and quantitatively, is evident when the character of such products as are included under the general term ptomaines and leucomaines, also tuberculin, antitoxine, etc., are consid-

ered. A knowledge of the gaseous products and the conditions under which they are formed is often of great service to the biologist in identifying different species. This is well illustrated by a condensed statement taken from an article by Dr. McWeeney in "Modern Medicine and Bacteriological Review," Vol. 8, August, 1894.

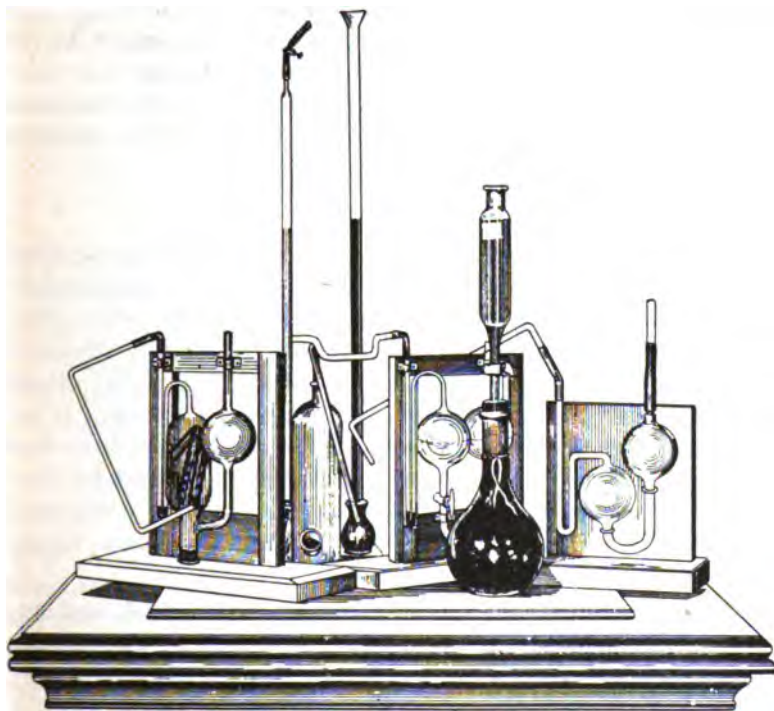
Dr. McWeeney says in this article that he made a study of the microbic cause of an epidemic of typhoid fever, which had recently occurred in the village of Waterford, England, using the method of Pariettis, Globis, and others. He identified the microbes as those of Eberth's, (that causing typhoid fever) while the fermentation test of Dr. Theobald Smith, of Washington, indicated on the contrary that the bacillus was not that of Eberth, but was the bacillus coli, since it produced decomposition of lactose, although not quite so freely as another specimen of bacillus coli with which it is compared. The bacillus of Eberth's did not, however, produce decomposition of lactose as does the bacillus coli.

It is a well known fact that micro-organisms, when surrounded by the conditions favorable to their growth, namely, a proper food supply, moisture, favorable atmospheric conditions, and temperature, develop very rapidly for a time. However, after a certain period the rate of development diminishes until finally it ceases entirely, although there may be a large supply of food material still unused and the general conditions have not changed. For example, the saccharomyces produces alcohol from sugar until about fifteen per cent. of the media becomes alcohol, when action practically ceases. A twenty per cent. solution of alcohol is antiseptic. Many illustrations for the effect on the growth of bacterial forms might be adduced, but they are too familiar facts to be repeated here.

In a study made by the authors an attempt was made to accurately estimate the constituents of the mixed gaseous products by a variety of bacteria. Hempel's apparatus was used for the estimation of the gases. The pieces employed are shown in the cut that accompanies this article.<sup>1</sup> The culture flask is the only apparatus that needs description. It consists of a half liter flask

<sup>1</sup> See Hempel's "Gas Analysis" for description.

closed with a three-holed rubber stopper, through one of the openings of which is passed the stem of a 100 cc. separatory funnel until it nearly reaches the bottom of the flask. Into the



second opening is inserted a fine capillary tube, bent at right angles, which serves to conduct the gas to the mercury gasometer. The third opening serves for the thermometer when temperature determinations are made. The flask is connected with the mercury gas-holder when ready for the connection of the gases.

The separatory funnel was used for inoculating the medium. The method of procedure is as follows: The flask is filled nearly full of the food medium which had been properly sterilized. The separatory funnel, which was filled about two-thirds full of the sterilized medium, was now inserted and the whole resterilized.

The stopper was next crowded in and the stopcock opened. The medium in the funnel was allowed to run into and fill the small vacant space below the stopper and force the liquid through the capillary tube until the latter is filled over to the mercury. The stopcock was then closed and the apparatus was ready for the collection of the gases. From the gas-holder the gas was transferred to the burette and the analysis carried on in the usual manner, except that mercury was used in the burettes instead of water.

#### PREPARATION OF THE MEDIA.

The fluid in all cases was peptone bouillon containing either glucose, lactose, or cane sugar. The bouillon was prepared by using either 250 grams of finely chopped lean beef, or five grams of Liebig's extract. After the meat was thoroughly cooked it was filtered, and to the filtrate was added five grams of salt, twenty grams of sugar and ten grams of dried peptone. It was then made up to a liter. The medium was now put in a flask and separatory funnel as before directed and sterilized for three successive days in a Kock's steam sterilizer, when it was ready for use. The Liebig's extract was treated in the same manner as was the meat extract.

The bacteria in all cases were taken from fresh cultures, grown either upon agar-agar, gelatin or potato. The medium in which the bacteria grew was in all cases neutral.

The following are the tabulated results of a few of the gas-producing organisms of which a study was made :

TABLE NO. I.—*BACILLUS AROMATICA*.

Temp.	Date.	Kind of sugar:	Gas present after days.					No. cc. taken.	Carbon dioxide. Per cent.	Hydrogen. Per cent.
			1	2	3	4	5			
1. 28°	July 23	Glucose.	o	87.5	173.	237.0		38.4	26.04	73.9
18°	Oct. 1	Glucose.	o	...	...	...	45.4	15.7	26.68	73.3
2. 28°	Aug. 2	Cane....	o	39.5	...	93.8	122.9	18.7	23.5	76.4
24°	Aug. 17	Cane....	o	...	...	...	...	32.2	21.8	78.0
3.	Aug. 10	Lactose.	o	o	o	o	o	o	o	o
	Aug. 15	Lactose.	o	o	o	o	o	o	o	o

TABLE NO. II.—MICROCOCOCCUS FROM CHEESE.

Date.	Kind of sugar.	Gas present after days.					Carbon dioxide.		Hydrogen.
		1	2	3	4	5	No. cc. taken.	Per cent.	
July 29	Glucose....	0	0	0	0	0	0	0	0
Sept. 22	Glucose....	0	0	0	0	0	0	0	0
Aug. 2	Cane.....	0	0	0	0	0	0	0	0
Sept. 22	Cane.....	0	0	0	0	0	0	0	0
Aug. 20	Lactose....	0	0	0	0	0	0	0	0
Sept. 15	Lactose....	0	0	0	0	0	0	0	0

TABLE NO. III.—JONES ANACROBE.

Temp.	Date.	Kind of sugar.	Gas present after days.					Carbon dioxide.		Hydrogen.
			1	2	3	4	5	No. cc. taken.	Per cent.	
1. 28°	Sept. 6	Glucose..	76.6	134.6	....	...	...	24.3	27.8	72.1
	July 23	Glucose..	...	....	....	...	...	72.0	11.5	82.4
2.	Aug. 29	Cane ....	0	136.8	151.8	...	...	...	42.3	57.6
	July 8	Cane ....	...	....	....	...	...	85.0	44.7	55.3
3.	Aug. 6	Lactose..	0	0	0	0	.	0	0	0
	Sept. 15	Lactose..	0	0	0	0	.	0	0	0

TABLE NO. IV.—BACILLUS COLI COMMUNIS.

Temp.	Date.	Kind of sugar.	Gas present after days.					Carbon dioxide.		Hydrogen.
			1	2	3	4	5	No. cc. taken.	Per cent.	
1. 28°	Sept. 6	Glucose..	119.6	162.0	....	....	0	31.0	25.16	74.8
22°	Sept. 30	Glucose..	....	76.6	....	...	...	45.0	23.2	76.8
2. 24°	Aug. 17	Cane ....	0	7.5	34.0	40.1	0	37.0	34.3	65.4
22°	Oct. 15	Cane ....	0	....	....	5.2	...	28.0	31.6	68.4
3. 26°	Aug. 27	Lactose..	0	....	....	76.6	233.5	27.0	28.8	71.1
	Oct. 19	Lactose..	0	....	140.1	...	...	35.3	27.2	72.8

TABLE NO. V.—BACILLUS COLI COMMUNIS.<sup>1</sup>

Kind of sugar.	Per cent. of gas present after days.							Total gas at 20°-25°.	Re- action of bulb.	Carbon dioxide.		Hydrogen.
	1	2	3	4	5	6	7			Per cent.	Per cent.	
Glucose .....	28.0	44.0	47.0	..	..	..	..	9 days. 44.	.....	32.0	68.0	
Cane .....	..	31.0	..	47.0	..	50.0	..	11 days. 43.	Acid.	36.5	63.5	
Cane .....	..	7.0	..	13.0	..	15.0	16.0	10 days. 19.	Alkali.	23.0	77.0	
Lactose .....	28.0	42.0	45.0	48.0	..	52.0	..	45.0	.....	37.0	35.0	

<sup>1</sup> This table taken from Dr. Theobald Smith's work.

TABLE NO VI. *BACILLUS MESAENTERICUS VULGATUS*.

Temp.	Date.	Kind of sugar.	1	Gas present after days.						Carbon dioxide gen.		
				2	3	4	5	6	taken.	cc.	Per cent.	Hydrogen per cent.
22° C.	Oct. 2	Glucose..	o	o	o	o	o	o	o	o	o	o
24° C.	Oct. 7	Glucose..	o	o	o	o	o	o	o	o	o	o
25° C.	Sept. 15	Cane....	o	76.6	99.6	166.90	...	o	32.2	61.1	38.8	
22° C.	Oct. 15	Cane....	.	...	76.6	.....	...	.	32.0	63.7	36.3	
	Sept. 22	Lactose..	o	...	...	79.1	96.	.	22.8	23.5	76.5	

A bacillus from butter-milk, not yet named, was used to inoculate a glucose peptone medium. The results being negative so far as gas development goes they are not tabulated. Action began in the separatory funnel, in course of twenty-four hours, and gas was quite rapidly developed. No gas was found in the flask after standing for four days and until action had ceased in the funnel. An examination of the medium in the flask showed that it was very markedly acid, showing that decomposition had taken place. The result is of value only as it shows that this bacillus can develop in the same medium with or without air and that the products vary in kind and amount.

#### STATEMENTS AND OBSERVATIONS ON THE TABULATED RESULTS.

1. As before mentioned, the media were neutral in all cases and were peptone bouillon, to which were added the different sugars, as noted in the tables.
  2. The gas should not be analyzed until the action is about complete, owing to the fact of absorption of the carbon dioxide by the media. The first portions of the escaping gas were in the cases examined nearly pure hydrogen. Therefore in considering the total gaseous products the absorbed carbon dioxide should be taken into account. It was found that each cc. of the media absorbed on the average at ordinary temperatures eight cc. of carbon dioxide.
  3. The temperature of the media has a marked effect, as is well known, on the rapidity and the time necessary for the development of the gas.
- A difference of ten degrees made a difference of four days in the time of completing the action in the case of bacillus aromaticus.

4. It will be noticed that at the same temperature the action starts at different periods and that the maximum action occurs at different lengths of time from the time of inoculation.

5. Alcohol was produced by several of the bacteria studied. *Bacillus aromaticus* produced no alcohol, but did form lactic acid. The micrococcus from cheese produced no gas in any case, *i. e.*, not enough to more than saturate the media, although there was evidence of quite active growth.

6. The solutions were acid in all cases at the end of the action. Lactic acid was found in most cases.

7. Jones' anaerobe produced acetic and lactic acids with glucose, lactic acid, and only a trace of acetic acid with cane sugar. The alcohol was more abundant in the latter case.

8. *Bacillus coli communis* produced no alcohol, but did form lactic acid.

9. The *bacillus mesentericus vulgatus* rendered the media but slightly acid. No alcohol was produced.

10. It should be noted that the amount of carbon dioxide produced by the different micro-organisms studied varies with the kind of sugar used. See Table VI in reference to glucose and lactose. This evidently shows a smaller capacity to procure oxygen in one case than in the other.

11. Looking at the tabulated results under *bacillus aromaticus*, it will be seen that the organism produces gas in solutions of glucose and cane sugar, but it does not produce any gas in solutions of lactose sugar.

12. In comparing the total amounts of gases produced by different species of bacteria, it is seen that they are the most active in glucose media, with the exception of *bacillus mesentericus vulgatus*, which produces no gas in glucose media. This fact will serve to distinguish this *bacillus* from a larger number of others.

13. *Bacillus aromaticus* and Jones' anaerobe produce gas in solutions of glucose and cane sugar, but none in lactose sugar. *Coli communis* on the other hand produces gas in solutions of all three sugars, the largest amount of gas being produced in the lactose solution.

Where no record of gas production is made in the tables it

means that action practically ceased before this time was reached.

SOME OF THE INVESTIGATIONS, PRINCIPALLY OF GASEOUS PRODUCTS, OF THE GROWTH OF MICRO-ORGANISMS ARE SUMMARIZED HERE.

The following interesting conclusions from a study of stomach dilatation are drawn by Hoppe Seyler :

*First.* In not a few cases (thirteen out of twenty-two) there were present carbon dioxide and hydrogen.

*Second.* The formation of hydrogen depends on butyric ferment.

*Third.* The formation of this hydrogen goes on even when the fluid contents of the stomach reaches two per cent. of sodium chloride.

*Fourth.* By removal of sodium chloride there is usually a larger per cent. of carbon dioxide.

*Fifth.* By the yeast ferment carbon dioxide only is formed.

*Sixth.* Often the dilated stomach only contains the gases that have been swallowed.

Another very important investigation of the products of bacterial decomposition was made by Brieger, using the pneumococcus of Friedländer.

By growing this specific germ in suitable solution of grape or cane sugar, he obtained principally acetic, together with some formic and succinic acids and ethyl alcohol. The same products were also obtained by the growth of this organism in solution of calcium lactate and creatine. In bacillus ethaceticus the amount of alcohol and acetic acid stand to each other in virtually the same proportions as does that produced by bacillus pneumococcus, yet the absolute amounts produced are much less than in that of the latter.

There is often some difference in the day when fermentation begins, but Frankland, Stanley and Frew remark that (although there is some difference in the several series of experiments as to the precise period which elapses between the time of inoculation and the commencement of fermentation) the balance of evidence points to the glucose being the least, and to the mannitol and cane sugar being the most fermentable. In the glucose fer-



mentation of pneumococcus the proportion of hydrogen to carbon dioxide by volume shows that the gases are given off in approximately the same number of molecules of each, but when mannitol was used ten molecules of hydrogen to twelve molecules of carbon dioxide were produced. This larger proportional evolution of hydrogen in the case of mannitol is what might have been anticipated from a consideration of the larger per cent. of hydrogen in mannitol.

Gartner also made some very interesting investigations. He studied mainly one bacterium, which he called a new gas-producing pathogenic bacillus. He inoculated different media containing varying quantities of sugar and peptone, also media showing different reactions. Different products and different proportions of products were obtained in most cases. He states that a three per cent. glucose medium gives a relatively larger per cent. of gas than a one and one-half per cent. solution; also that an acid reaction hinders the production of gas and the total amount of gas is not as much as was formed from the same solution when it was neutral.

Another investigator of the gases produced by bacteria deserves mention, namely, Dr. Theobald Smith, of Washington.

Dr. Smith, in his analysis, used a fermentation tube devised by himself. The media and fermentation tubes were completely sterilized, after which the media was inoculated with specific germs. The gas was afterwards determined by using potassium hydroxide as an absorbing material for the carbon dioxide. The remainder of the gas he calls an explosive gas and assumes it to be hydrogen.

The types of bacteria which he took were bacillus coli communis, hog cholera bacillus, B. lactis aerogenes, bacillus of Friedlander, B. aedematis maligni, proteus vulgaris, B. cloacea and saccharomyces.

The result of his study of these micro-organisms was to show that the media conditions under which development took place modified the proportion of the gaseous products and the rapidity of their formation. His results also show that these facts may be used to a marked extent to determine species.

The following is a short bibliography of this subject.

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## CHEMICAL VS. BACTERIOLOGICAL EXAMINATION OF POTABLE WATER.<sup>1</sup>

BY W. P. MASON.

Received November 16, 1895.

**A** PROPOS of the recent articles upon this question, which have appeared in the English papers, it is noteworthy that there is a growing tendency among physicians and civil engineers to belittle the chemists opinion regarding the potability of a water, and to pin their faith exclusively upon what the bacteriologist may have to say upon the subject. This feeling is strengthened by the publication of the results of such trials as that undertaken by the London Local Government Board, in which it will be remembered, water samples purposely inoculated with typhoid germs, were sent for analysis to one of England's leading chemists and were by him pronounced pure.

Those who set special value upon such a "test" of methods as the above, and who consider it quite final as showing the

<sup>1</sup> Read before the New York Section.

inability of chemistry to detect pollution in a liquid which the bacteriologist would instantly pronounce very foul, should remember that such a sample of water could not be found in practice, and that the very conditions under which it was prepared, eliminated the chemical items indicating pollution, while it increased tremendously the signs governing the bacteriological side of the case.

The bacteriologist sought for the Eberth bacillus, and very naturally, quickly found it in a water purposely sown with a culture of the germ.

The chemist looked for those elements which always occur in sewage-laden water, whether the sewage be from sources of disease or otherwise, and, not finding them, he pronounced the water to be what it really was, free from sewage addition.

Sewage, as it occurs in practice, contains an immense deal of material other than that productive of disease, and it is upon just this comparatively harmless, but constantly present material that the chemist relies for the indication upon which he bases his opinions.

He is unable to say whether or not a sewage-laden water is disease-bearing on any particular date, for to him all sewage is alike, but he condemns the water, for the reason that, although it may be harmless to-day, it is impossible to predict what may be its condition to-morrow.

Within the week, I have been requested to make a bacteriological examination of the water of a certain well, in order to determine if it be affected by neighboring cesspools.

The physician who made the request was impressed with belief in the paramount value of such an examination and the comparative uselessness of chemical analysis.

I am quite convinced that, had I followed his suggestion, I should have sought in vain for any specific microbe, but inasmuch as upon chemical analysis, I found that the "chlorine" ran twenty-four parts per million, which is about ten times the local "normal," and the "nitric nitrogen" read nine parts per million in place of 0.116, I condemned the water off hand without going further.

There is simply no comparison between the two methods in

question for water problems of this class, and the value of chemistry is still more pronounced in those instances where it is possible to introduce common salt or lithium chloride into a source of suspected pollution, and then look for increased chlorine or presence of lithium in the water of the well. In legal cases touching upon this point of contamination of wells, by cemeteries for instance, the chemical testimony is especially strong.

In the matter of determining the suitability of a stream for city supply, the services of the bacteriologist should be unquestionably secured, but it is doubtful if his report can be considered of more importance than that of the chemist.

Chemical analysis, by comparing the water taken at the site of the proposed intake with that from the same stream above all points of possible pollution, can indicate whether or not up stream contamination is felt at the lower point; nor is it necessary that the polluting sewage be from pathogenic sources in order that its presence may be recognized.

As Dr. Dupré has pointed out, chemistry in such cases anticipates what may happen in the future, and, by timely advice, may prevent an outbreak of disease, while, on the other hand, the discovery of disease germs in a water is only possible after the water has become infected.

Bacteriology is of especial value, and greatly superior to chemistry, for the testing of filters and watching any variation in their efficiency.

For this purpose the simple count of germs per cc. is most valuable, and differentiation is a secondary matter; for the assumption is a just one, that a filter which will remove the harmless bacteria, will take out the objectionable ones as well.

It is very far from my desire to decry the value of bacteriology, but I cannot but feel, that in their enthusiasm over the great triumphs of the new science, the people at large have gone slightly "bacteria mad," and are apt to expect more than can be furnished by the means and information now available.

## THE ELECTROLYTIC ESTIMATION OF MERCURY.

BY EDGAR F. SMITH AND DANIEL L. WALLACE.

Received November 29, 1895.

THE precipitation of this metal from a cyanide solution<sup>1</sup> has given quantitative results, which render the electrolytic procedure decidedly more advantageous to the analyst than the usual gravimetric course. However, conditions sometimes occur when even the preceding rapid method is made time-consuming. Thus in the working with mercury sulphide it would be necessary to first dissolve the substance in acids and remove the excess of the latter before advancing to the electrolytic decomposition of the resulting salt. Conscious of this fact and that mercury sulphide, as cinnabar, is a natural product, which is quite often offered for analysis, we took occasion to review the method first proposed by Smith,<sup>2</sup> and subsequently confirmed by Vortmann,<sup>3</sup> viz., the electrolytic deposition of mercury from its solution in an alkaline sulphide. The chief point to be ascertained was whether the time factor could be reduced. This had been accomplished with the cyanide solution by simply applying a gentle heat, thereby precipitating two-tenths gram of metal in about two hours. Another point which we wished to definitely establish was the exact current density for a given electrode surface. To this end several determinations were made, using a mercuric chloride solution of known mercury content :

Mercury present as chloride. gram.	Mercury found. gram.	N. D. of current in amperes for 100 sq. cm. surface.	Dilution of solution. cc.	Time.	Temp.
0.1913	0.1917	0.13	125	3 hrs.	65°
"	0.1916	"	"	"	"
"	0.1908	"	"	"	"

In each case twenty cc. of sodium sulphide of specific gravity 1.22 were present.

These results indicate that mercury can be determined as rapidly and as accurately in this way as when working with a cyanide solution.

<sup>1</sup> This Journal, 17, 612.<sup>2</sup> J. Franklin Inst., 1891, and J. Anal. Chem., 5, 202.<sup>3</sup> Ber. d. chem. Ges., 24, 2749.

We next determined the mercury in a sample of cinnabar by distilling the latter with lime, collecting and weighing the metal as directed in Fresenius' Quantitative Analysis, Am. Ed., p. 306.

1. 0.9590 gram of mineral gave 0.8194 gram of metal, or 85.44 per cent.

2. 0.8586 gram of mineral gave 0.7325 gram of mercury, or 85.31 per cent.

Portions of the same mineral were weighed out in platinum dishes and after solution in twenty to twenty-five cc. of sodium sulphide of specific gravity previously mentioned, were diluted with water to 125 cc. and electrolyzed at a temperature of 70°, with a current of  $N. D_{100} = 0.12$  ampere. The period of time allowed for the precipitations never exceeded three hours. The results were :

	Cinnabar. gram.	Mercury. gram.	Percentage.
1.....	0.2167	0.1850	85.37
2.....	0.2074	0.1769	85.29
3.....	0.2432	0.2077	85.40

We would observe that during the electrolytic decomposition the platinum dishes should be carefully covered to prevent evaporation, thereby exposing a rim of metal, which if not in part volatilized, would yet be changed to mercury sulphide. The latter is indicated by a dark-colored film. With a little attention there should be no question as to the final outcome of any determination made in this way. We regard the method as entirely satisfactory. The short time required for a determination, as outlined above, will recommend it in our judgment to analysts generally.

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## THE PRECIPITATION OF PHOSPHOMOLYBDATE IN STEEL ANALYSIS.

By GEORGE AUCHY.  
Received December 2, 1902.

IN a recent paper<sup>1</sup> Messrs. Blair and Whitfield give a new formula for the preparation of molybdate solution, which is a great improvement on the old one, as by its use the separation of

<sup>1</sup> This Journal, 15, 24.

ammonium molybdate from the solution by long standing is avoided and the solution retains its strength. In using solution of the new formula, however, the writer, a number of times, has had a further precipitation of phosphomolybdate to occur after filtration. This additional precipitate could not have resulted from insufficiency of molybdate solution—sixty to seventy-five cc. of the solution having been used; nor from insufficient shaking—ten minutes having been given in each case. The precipitation seemed to be the result of the dilution of the liquid by the wash water, and not of the longer standing, as in several cases the original phosphomolybdate precipitate had stood an hour or more, and in one case, all night before filtering. This seemed an indication that dilute solution is a help to complete precipitation. But the query then arose, Why had this after separation of phosphomolybdate never occurred before in using molybdate solution of the old formula? The explanation at once suggested itself. Because when solution of the old formula is used the amount of ammonium nitrate present is necessarily much larger. If these assumptions are correct, it then would seem that the presence of ammonium nitrate and a dilute solution are both important factors in the thorough precipitation of the phosphomolybdate (the former is, indeed, a well known fact). Acting upon this hint, precipitations have since then taken place in solutions of larger volume, and containing a greater proportion of ammonium nitrate; effected by increasing the volume of nitric acid (sp. gr. 1.13, recommended by Drown), as used for solution of two grams steel, to 100 cc., and the amount of strong ammonia used for neutralization, to fifteen cc. diluted with fifty cc. cold water. The following few experiments which the writer has had time to make, give some corroboration to this theory.

*Experiment 1.* Heat 369. 1. Solution nearly neutral. Volume small. Considerable ammonium nitrate present. Sixty cc. nitric acid (1.13) for solution of the steel. Eight cc. strong ammonia for neutralization. Thirty-five cc. molybdate solution of old formula, —0.009 per cent.

2. Solution very strongly acid. Dilute in volume. Large excess of ammonium nitrate present. One hundred cc. nitric acid (1.13) for solution. Fifteen cc. strong ammonia for neu-

tralization. Then fifty cc. strong nitric acid, and fifteen to twenty grams of crystallized ammonium nitrate. Sixty cc. of molybdate, new formula,  $-0.010$  per cent.

*Experiment 2.* Heat 352. 1. Solution nearly neutral. Volume dilute. Considerable ammonium nitrate present. One hundred cc. nitric acid (1.13) for solution. Fifteen cc. strong ammonia for neutralization. Sixty cc. molybdate solution of new formula,  $-0.161$  per cent.

2. Solution very strongly acid. Volume dilute. Large excess of ammonium nitrate present. One hundred cc. nitric acid (1.13) for solution. Fifteen cc. strong ammonia for neutralization. Then fifty cc. strong nitric acid, and fifteen to twenty grams of crystallized ammonium nitrate. Sixty cc. molybdate solution of new formula,  $-0.160$  per cent.

These results tend to show that rather large dilution and plenty of ammonium nitrate are important conditions in the complete precipitation of the phosphomolybdate, and that the degree of neutralization of the nitric acid before precipitation is unimportant, the complete precipitation depending, not upon the approximate neutralization of the liquid, but upon the amount of ammonium nitrate present and the dilution of the solution. The reverse of this (solution small in bulk and nearly neutral) is sometimes recommended.<sup>1</sup> As before stated, about the right dilution and the proper amount of ammonium nitrate seems to be obtained by using one hundred cc. nitric acid of specific gravity 1.13 for solution of the steel, and fifteen cc. strong ammonia in fifty cc. cold water for neutralization previous to the addition of the molybdate solution. But if it be desired to have the solution less in volume, this amount of ammonium nitrate will not always suffice, as the writer has found by experience. The dilution seems to be an important requisite when molybdate of the new formula is used.

The amount of phosphorus precipitating after filtration, in the cases referred to (determined as pyrophosphate to guard against the contingency of the separation being ammonium molybdate merely), was respectively 0.020, 0.003, and 0.013 per cent.

As showing the very great degree of error that may occur

<sup>1</sup>This Journal, 19, 23.



from the careless use of molybdate solution of the old formula, the following results may be of interest to members of the society.

The molybdate solution had been made up for two—possibly three or four weeks. Then a close-down of the works for three weeks for repairs, at the end of which time the use of the solution was thoughtlessly resumed. But the extreme lowness of the results for heats 307 and 308 threw suspicion upon the solution, and duplicate determinations were made with fresh solution and continued till complete demonstration was had that the molybdate solution was at fault.

		With old solution. Per cent.	With fresh solution. Per cent.
Heat	306.....	0.048	0.060
"	307.....	0.004	0.006
"	308.....	0.002	0.006
"	309.....	0.033	0.035
"	310.....	0.013	0.020
"	311.....	0.002	0.007
"	312.....	0.002	0.006
"	313.....	0.001	0.008
"	314.....	0.012	0.036
"	315.....	0.010	0.049
"	316.....	0.001	0.007
"	317.....	0.008	0.049
"	318.....	0.002	0.020

Many authorities advocate the taking of the temperature of the liquid before the addition of the molybdate solution; or the precipitation of the phosphomolybdate at a certain exact temperature—85° usually. The writer ventures to question whether, in a busy iron or steel works laboratory, it is worth while to take this trouble. For if five minutes be allowed for cooling after the solution is withdrawn from the flame, or if the flask be plunged into cold water a couple of times, there is no danger of its temperature being over 85°; and Babbitt has shown that down to 25° all the phosphorus precipitates. Doolittle habitually precipitates at 35° to evade arsenic. Another authority (Johnson, I think) avoids a temperature higher than 50° to prevent oxides of iron and alumina from precipitating with the phosphomolybdate. So that where arsenic is not present any temperature

between the wide limits of  $25^{\circ}$  and  $85^{\circ}$  is all right, and one can not err in omitting the use of the thermometer altogether. The iron is not likely to precipitate if the solution be acid enough. Nevertheless a temperature below  $50^{\circ}$  is perhaps better than one higher.

As a reducing agent, perhaps the majority of chemists follow Jones in favoring ferrous sulphate. The writer found considerable phosphorus<sup>1</sup> in a lot of nice clean looking sulphate labelled "Free from phosphorus," and has since then used sugar as originally recommended by Dr. Drown. The queerest experience in the way of impure chemicals was the finding of phosphorus in "C. P." nitric acid—enough to add 0.06 per cent. to the real percentage in the steel. A second bottle from the same makers also contained it, though not in so great amount.

### THE USE OF THE CALORIMETER IN DETECTING ADULTERATIONS OF BUTTER AND LARD.<sup>2</sup>

BY E. A. DE SCHWEINITZ AND JAMES A. EMERY.

Received January 3, 1896.

WHILE engaged in a study of the comparative value of butters and oleomargarines, it occurred to one of us that possibly the determinations of their respective heats of combustion might be useful if taken in connection with other data. Prof. Atwater, who has for some time been conducting experiments with an improved calorimeter, very kindly consented to burn such samples as might be sent to him. The first results were so interesting that it occurred to us at once that this method might be useful in detecting the adulteration of butter with oleomargarine, and also perhaps in distinguishing between lards of different sources and compound lards. Accordingly, some specially selected samples of which duplicates were kept in our laboratory, were sent to Prof. Atwater, and in the case of the butters and oleomargarines the results confirmed our first suppositions. In the use of the lards, however, the results were not so sharply distinctive, but taken in conjunction with other analytical data will prove, as we will endeavor to show,

<sup>1</sup> Not enough, however, to affect the results very seriously. 0.111 per cent. instead of 0.105 per cent., for instance; and 0.056 and 0.054 per cent. in another steel.

<sup>2</sup> Read at the Cleveland meeting, Dec. 31, 1895.

TABLE I.  
ANALYSES OF BUTTERS AND OLEOMARGARINES.

No.	Manufacturer.	Specific grav- ity at 100° C.	Water, per cent.	Vol. $\frac{n}{D}$ Ba(OH) <sub>2</sub> for 2.5 grams.	Salt, per cent.	Casein, per cent.	Ash, per cent.	Melting point, °C.	Iodine equivalent.	Combustion calories per gram. At water.	Cottonseed-oil, Bechi's test.	Coloring matter.	Sample No.
1	Oakdale Mfg. Co., oleomargarine	0.916	8.09	0.30	4.02	1.46	4.24	62.19	62.19	No reaction.			1
2	Vermont "	0.908	10.96	0.17	6.60	1.43	4.68	63.52	66.69				2
3	" "	0.907	9.32	0.25	4.80	1.36	6.01	61.44	62.83				3
4	Woodlawn Dairy Co.,	0.913	9.40	0.15	5.40	0.97	4.83	63.26	60.62				4
5	Oakdale Mfg. Co.,	0.911	9.86	0.17	6.80	0.88	3.38	59.11	62.83	No reaction.			5
6	Oakdale Mfg. Co.,	0.890	9.81	0.20	5.52	1.44	4.77	60.62	62.83	Slightly dark.			6
7	Vermont "	0.896	8.52	0.55	4.43	1.41	5.95	62.80	60.05	Purple brown.			7
8	Oakdale "	0.885	8.53	0.42	5.17	1.36	2.96	60.05	63.12	No reaction.			8
9	" "	0.886	10.69	0.27	2.99	1.21	5.29	64.49	66.50	Purple brown.			9
10	" "	0.894	7.37	0.35	3.75	1.16	5.29	64.49	66.50	Purple brown.			10
11	" "	0.896	8.00	0.35	3.42	1.77	5.67	66.50	66.50	No reaction.			11
12	Vermont "	0.894	9.47	0.45	5.31	1.33	4.49	66.50	66.50	Purple brown.			12
13	" "	0.898	9.73	0.45	4.36	1.53	4.49	66.50	66.50	No reaction.			13
14	" "	0.887	9.00	0.30	3.68	1.66	4.49	66.50	66.50	Purple brown.			14
15	Woodlawn Dairy Co.,	0.897	9.23	0.35	3.97	1.47	3.76	60.67	60.67	Slight dark ng			15
16	Swift & Co.,	0.892	8.32	0.22	2.12	0.81	2.19	60.67	60.67	No change.			16
17	Woodlawn Dairy Co.,	0.889	9.15	0.22	6.69	1.43	6.21	60.67	60.67	Highly colored			17
18	Hammond,	0.889	9.25	0.27	4.04	0.77	4.04	60.67	60.67	Vy highly colored			18
19	Brown, Fitzgerald & Co.,	0.886	9.87	0.82	5.22	1.54	5.70	60.67	60.67	" "			19
20	Woodlawn Dairy Co.,	0.888	9.23	0.15	3.80	1.53	5.18	60.67	60.67	No reaction.			20
21	" "	0.883	10.68	0.22	5.63	1.53	5.18	60.67	60.67	Highly colored			21
22	" "	0.893	9.37	0.22	5.82	1.63	5.42	60.67	60.67	No reaction.			22
23	Goshen Mfg. Co.,	0.898	8.32	11.10	8.55	1.47	3.64	60.67	60.67	" "			23
24	Highland Creamery, butter	0.897	8.55	10.82	4.05	1.84	4.93	60.67	60.67	No reaction.			24
25	Plains, Va.,	0.894	12.98		4.04	1.30	3.94	60.67	60.67	" "			25
26	Armour & Co., beat "									No reaction.			26
27	" " cheap "									" "			27
28	" " cheap "									" "			28
29	Elgin and Woodlawn No. 28									No reaction.			29
30	" " "									" "			30
31	" " "									" "			31
32	Greensboro, N. C., sample 1									" "			32
33	Called butter.									" "			33
34										" "			34

exceedingly useful. The samples were forwarded to Prof. Atwater, prepared for combustion, without any description of their character being given except that they were fats. It is well understood that the estimation of the calories is of considerable use in a determination of the molecular weights of complex molecules and the results which we will report will serve to show, we think, practical application of the use of the bomb calorimeter.

This is best seen by a study of the following tables, which give in detail the examinations that are ordinarily made for oleomargarine and butter (Table I.), and accompanying these examinations the calories per gram. The samples were prepared for these latter determinations by washing, melting, filtering, and drying the samples at 100° C.

The figures given by different authorities for butter fat, vary slightly. Stohman gives the heat equivalent as determined by the potassium chlorate method as 9.192 small calories per gram, while by the oxygen method it was 9.231 calories per gram. The three samples of pure butter burned were from the following sources: No. 28, the best butter used by Armour & Co., in the manufacture of butterine. No. 26, was Elgin Creamery butter, and No. 27, obtained from a Virginia gentleman, who sent it as a sample of the best butter made on his place. Nos. 31, 32, and 33, were mixtures of Elgin butter and oleomargarine. The figures obtained for butter fat are a little higher than those Stohman gives for pure butter.

*Table II.* The steady increase in the calories of the mixtures is in proportion to the amount of oleomargarine added to the butter and this taken in conjunction with the iodine number gives additional confirmatory evidence of the character of the sample.

TABLE II.

MIXTURE COMPOSED OF DEFINITE PROPORTIONS OF ELGIN AND WOODLAWN No. 2<sup>3</sup>.

Sample.	Actual iodine equivalent.	Theoretical iodine equivalent.	Actual combustion calories per gram.	Theoretical combustion calories per gram.
$\frac{1}{2}$ E and $\frac{1}{2}$ W, No. 2 <sup>3</sup> ...	43.90	43.76	9.391	9.412
$\frac{1}{3}$ F and $\frac{2}{3}$ W, No. 2 <sup>3</sup> ...	48.01	49.77	9.416	9.498
$\frac{1}{4}$ E and $\frac{3}{4}$ W, No. 2 <sup>3</sup> ...	55.40	55.78	9.491	9.584

The theoretical calories per gram for the above mixtures as compared with those found are,

	Theory.	Found.
No. 31.....	9.412	9.391
No. 32.....	9.498	9.416
No. 33.....	9.584	9.491

The actual combustion of the sample containing a small admixture of oleomargarine falls a little lower than theory requires, but is sufficiently high to indicate at once that there is adulteration of the normal butter. The other two samples give results still more distinctive and characteristic. The determination of the calories would be sufficient, therefore, to detect oleomargarine. If not relied upon entirely it still furnishes very satisfactory evidence. One point to which attention should be called is the exceedingly low temperature at which the oleomargarines melted. They were purchased at the end of winter and probably made to suit the winter trade. If left in an open dish in the laboratory for a few hours they became soft and semi-fluid.

In the case of the lards from various sources the results are somewhat different and are not so distinctive as compared with compound lard, as the butter and oleomargarine. (Table III.) Still even here the determination of the calories taken in conjunction with other determinations, as the iodine absorption, will also be of use. Should the determination of the calories show a low figure one could conclude that the lard was either a compound or a lard from the caul, intestines, or head of the animals, while the determination of the iodine number and cotton-seed-oil test, would show at once whether the sample was a lard or a compound lard. The error of experiment in calorimetric work is usually counted at twenty-five calories per gram, but by careful work can be made less and a number of experiments in the same line as the above, would probably give data that would make the determination of the calories of still more practical value.

TABLE III.

## ANALYSES OF SPECIMENS FROM ARMOUR &amp; CO.

Quality.	Melting point.	Iodine equivalent.	Combustion calories per gram.	Cotton-seed oil, Bechi's test.
Lard, leaf.....	....	56.85	9.621	none.
" caul fat ....	40.0 <sup>c</sup>	58.61	9.573	Slightly darken
" intestinal fat	40.7 <sup>o</sup>	54.74	9.581	" "
" heads .....	29.5 <sup>o</sup>	68.79	9.503	None.
" mixture of all fats...	....	63.86	9.654	"
" trimmings .	....	65.57	9.606	"
" compound, 1st grade.	....	86.18	9.583	Purple brown.
" compound, 2nd grade	....	86.57	9.530	" "
" shield .....	....	61.01	9.598	None.
" special pure	37.5	63.63	9.617	"

In a recent number of this Journal, September, 1895, Wesson has very carefully reviewed the subject of the determination of the iodine absorption number in pure and compound lards, claiming that the figures heretofore given for pure lard were too low for the present methods of manufacture. This point also came up for incidental consideration in connection with our other examinations. We secured two sets of samples from Chicago, one sent direct from Armour & Co. (Table III), with the statement that the samples were what the names indicated. The other set of samples was accompanied by a certificate from the inspector testifying to the character of the material as forwarded.

TABLE IV.

## ANALYSES OF LARDS FROM ARMOUR &amp; CO.

Quality	Iodine equivalent	Cotton-seed oil, Bechi's test.
Leaf .....	56.85	No reaction.
Caul fat.....	58.61	" "
Intestinal fat.....	54.74	" "
Heads.....	68.79	" "
Trimming.....	65.57	" "
Special pure.....	63.63	" "
Foreign shield.....	61.01	" "
Exp. Ref. Comp.....	86.57	Purple black.
Prime steam.....	86.18	No reaction.
Doin. comp.....	86.57	Purple black.

TABLE V.

Sample.	Iodine equivalent.	Cotton-seed-oil. Bechi's test.	Combustion calo- ries per gram.
Lard No. 5 .....	58.98	....	....
Lard Plains.....	50.49	....	9.606
Cottolene .....	90.89	Purple black.	....

In addition two other samples of lard, one from Virginia, the other from Rhode Island, were examined. The samples sent with the inspectors' certificate were freshly made, while the other set was older material. There is a decided variation in the iodine equivalent and in deciding upon the character of the lard, the origin of the sample should undoubtedly be taken into consideration. As this is often not possible a check upon the other results may be secured by the determination of the calories.

BIOCHEMIC LABORATORY, WASHINGTON, D. C.,  
December 14th, 1895.

*Discussion.*—Mr. A. H. Sabin: I am very decidedly of the opinion that in investigations as to fats and oils, conclusive and satisfactory results can only be obtained by a comparison of methods. Such a method as this seems to me to be of a good deal of practical value because it is definite and positive. We make a combustion in this way and get some results which can be depended upon, and which can be verified; and the conditions are not difficult to duplicate. While I doubt if such a method will be of permanent value, because in such matters the ingenuity of the manufacturer is always pitted against the skill of the analyst, such a method always has weight, and must be taken in conjunction with other methods which also have weight and which also by themselves are not conclusive, but which have cumulative effect. I am certain that in regard to the vegetable fats it is only possible to arrive at just conclusions by a comparison of methods.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE. NO. 16.]

# NOTE ON THE USE OF ACETYLENE GAS AS AN ILLUMINANT FOR POLARISCOPIC WORK.<sup>1</sup>

By H. W. WILEY.

Received November 23, 1895.

THROUGH the courtesy of Prof. Charles E. Munroe, I was able to secure twenty-five kilos of calcium carbide for

<sup>1</sup> Presented to the Washington Section, Dec. 9, 1895.

experimental purposes, together with four burners. The acetylene was developed by the action of water on the calcium carbide and conducted into a small gas meter from which it was burned under a pressure of water, the flame being regulated by a stop-cock. The quantity of gas furnished by the calcium carbide is illustrated by the following experiment :

From ninety-five grams of carbide 11.5 liters of gas were obtained measured at a temperature of  $18^{\circ}$ . It is thus seen that one kilo of the calcium carbide used would furnish a little over 226 liters of gas.

The rate at which the gas was burned for furnishing the illumination for the polariscope was measured and found to be one liter each four minutes, measured under a pressure of thirty inches of water. The actual pressure at which the gas was burned was very much less than this, being regulated by the stop-cock. The lamp was thus supplied at a rate of consumption amounting to fifteen liters per hour.

The illumination produced by the burning acetylene was used with a triple shadow Schmidt & Haensch double compensating polariscope and the accuracy of the readings with the intensely white light produced was tested with standard quartz plates. Two of the quartz plates read were standardized by the U. S. Coast and Geodetic Survey, in connection with this Division, and four were standardized by the Imperial German Commission of the Physical Institute at Berlin. The readings, to the nearest whole tenths, were as follows, at a temperature of  $20^{\circ}$ , which is slightly higher than that at which the quartz plates were standardized :

Coast Survey tube	92.06	read	92.1
" "	99.06	"	99.1
German tube	74.45	"	75.4
" "	93.59	"	93.6
" "	100.36	"	100.3
" "	—91.70	"	—91.7

From the above readings it is seen that the light is absolutely reliable as tested against the best standards.

The degree of illumination was very great. The field of vision of the polariscope showed an intense illumination even at the neutral point and yet permitted of the reading of the shadow at



the neutral point with the greatest accuracy. Three different observers in reading the quartz plates did not differ among themselves more than one-tenth of a degree.

A test was also made to determine the relative possibility of reading highly colored solutions with the acetylene light as compared with the ordinary kerosenes or gas illumination for the polariscope. A solution of "black strap" molasses was made, quite concentrated, without any clarifying agent whatever other than lead subacetate. The solution read in a 200 and 400 mm. tube gave a perfectly distinct shadow with the acetylene light permitting the reading to within one-tenth of a degree. With the kerosene or lamp light, the field of vision was almost obscured at the neutral point and the readings made by three different observers differed as much as three-tenths of a degree. Another solution was made with the same black strap molasses without the use of any clarifying agent other than alumina cream. This was diluted to such a degree as to be distinctly read to within one or two-tenths of a degree by the acetylene light. When an attempt was made to read this same solution by the ordinary source of illumination, it was found that the field of vision was absolutely obscured, no light whatever passing through.

The results of these observations show that the acetylene light is perfectly reliable for polarizing purposes, that it produces an intense degree of illumination permitting of a very delicate distinction between the shadow and the illuminated portions of the field of vision, and permits the reading of solutions so highly colored as to be perfectly opaque to the ordinary sources of light.

The above results suggest also the practicability of using the acetylene light for microphotographic purposes and for ordinary photography, but I have not made any tests of its actinic power. The light can also be used for projections. It is to be observed that with the small quantity of calcium carbide obtained, *viz.*, twenty-five kilos, there would be a sufficiency for almost a continuous polarization through a long period of time. With the cost of the calcium carbide known the actual cost of the light could be easily computed. I am ignorant, however, of the cost

of the calcium carbide, it having been obtained for our use by the payment of the express charges only.

My thanks are due to Messrs. McElroy, Ewell, and Runyan for assistance in the preparation of the gas and in reading the polariscope.

### INDIRECT ANALYSIS.

BY EDWARD K. LANDIS.

Received December 23, 1895.

IN investigating this subject the author was struck with the difference in the formulas given in the text-books and on trying some of the cases found the results did not agree. Supposing that the old atomic weights used in the formulas were the cause of the trouble, it was thought best to derive a formula in such a manner that it would apply equally if the present weights should be modified, and it is given herewith, trusting that it may be useful to many chemists in cases where a separation of the two elements is difficult or tedious.

It will apply to any case where the atomic weights of the two elements are not the same, and the greater the difference between the atomic weights the greater the accuracy. Unfortunately, nickel and cobalt cannot be determined in this manner, but many other elements can be. This method is especially convenient for sodium and potassium, and probably more accurate than the separation with platinum chloride.

#### FIRST METHOD.

##### *Data given:*

Weight of mixture.

Weight of common constituent.

Let  $x$  = weight of salt with greatest per cent. of common constituent.

Let  $y$  = weight of salt with least per cent. of common constituent.

Let  $a$  = amount of common constituent in one part of  $x$ .

$b$  = " " " " " " " "  $y$ .

$W$  = weight of mixture.

$w$  = " " common constituent.

To find  $x$  and  $y$  :

$$\begin{aligned}
 x + y &= W, & x &= W - y, \\
 ax + by &= w, \\
 a(W - y) + by &= w, \\
 aW - ay + by &= w, \\
 by - ay &= w - aW, \\
 (b - a)y &= w - aW, \\
 y &= \frac{w - aW}{b - a}, \\
 x &= \frac{w - bW}{a - b}.
 \end{aligned}$$

$a - b$  = difference of coefficients of  $x$  and  $y$ .

Therefore, to find  $x$  or  $y$ , multiply the weight of mixture by the coefficient of the other salt. Find the difference between this and the weight of common constituent, and divide this result by the difference of the coefficients.

#### SECOND METHOD.

Same data as before and same symbols, except that here

$a$  = molecular weight of  $x$ .

$b$  = " " "  $y$ .

If all the common constituent were combined with  $y$  we should have a greater weight than  $W$ , and if combined with  $x$  less than  $W$ . In either case call this  $W'$ .

$$\begin{aligned}
 \text{Then } \frac{b}{a}x + \frac{b}{b}y &= W', \\
 \frac{a}{a}x + \frac{b}{b}y &= W, \\
 \hline
 \text{Subtracting } \frac{b-a}{a}x &= W' - W, \\
 x &= \frac{a(W' - W)}{b - a}, \\
 b - a : W' - W &= a : x.
 \end{aligned}$$

**Rule.**—Calculate the weight if common constituent were all combined with one of the salts. Find the difference between this and the weight of the two salts. Then the difference of the molecular weights is to the difference found as the molecular

weight of the salt causing the difference is to the amount of that salt.

As an illustration let us take two grams sodium chloride and one gram potassium chloride with the following data :

$$\begin{aligned}\text{Cl} &= 35.45 \\ \text{Na} &= 23.05 \\ \text{K} &= 39.11 \\ \text{KCl} &= 47.5456 \text{ per cent chlorine.} \\ \text{NaCl} &= 60.598 \quad \quad \quad \text{''} \quad \quad \quad \text{''}\end{aligned}$$

#### FIRST METHOD.

$$\begin{aligned}W &= 3, \\ w &= 1.687416, & x &= \text{NaCl}, \\ a &= 0.60598, & y &= \text{KCl}, \\ b &= 0.475456, \\ x &= \frac{w-bW}{a-b} = \frac{1.687416 - 1.426368}{0.130524} = 2, \\ y &= \frac{w-aW}{a-b} = \frac{1.81794 - 1.687416}{0.130524} = 1.\end{aligned}$$

Crookes gives the following formula :

Let  $W$  = weight of mixed chlorides.

$C$  = " " chlorine.

$$\text{NaCl} = C \times 7.6311 - W \times 3.6288.$$

$$\text{KCl} = W \times 4.6288 - C \times 7.6311.$$

Using the data above this gives  $\text{NaCl} = 1.9904$ ,  $\text{KCl} = 1.0096$ .

The above formula should read

$\text{NaCl} = 7.6311 C - 3.6288 W$  to be perfectly clear, otherwise it means that  $C$  is multiplied by 7.6311,  $W$  subtracted from the product and the result multiplied by 3.6288, which would not give the answer.

Bailey's Chemists Pocket Book (3rd edition) gives the following :

$$\text{NaCl} = ((C \times 2.1029) - W) \times 3.6288.$$

Using the same data this gives  $\text{NaCl} = 1.990277$  instead of 2.0.

#### SECOND METHOD.

Calculating Cl to KCl.

$$\text{Cl} = 1.687416,$$

$$W = 3,$$

$$\frac{1.687416}{0.475456} = 3.549047 \text{ KCl},$$

$$3.549047 - 3.0 = 0.549047,$$

$$\frac{0.549047 \times 58.5}{74.56 - 58.5} = \text{NaCl} = 2.$$

Calculating Cl to NaCl.

$$\frac{1.687416}{0.60598} = 2.7846 \text{ NaCl},$$

$$3.0 - 2.7846 = 0.2154,$$

$$\frac{0.2154 \times 74.56}{74.56 - 58.5} = \text{KCl} = 1.$$

The author hopes that this may prove the accuracy of the method and that it may be extensively used.

The preceeding applies to mixtures of two substances only ; now let us consider the case of three. If we have iodine, bromine and chlorine in the same liquid, how are we to arrive at the amounts of each? We may consider two cases, one given in Woodward's Chemical Arithmetic and the other in Crookes' Select Methods, the second being exactly the opposite of the first. Three equal portions of a liquid containing chlorine, bromine and iodine are taken. No. 1 is precipitated with silver nitrate and precipitate of silver iodide, silver bromide and silver chloride weighed. No. 2 is precipitated in the same manner, but digested with potassium bromide until all chlorine is replaced by bromine, then weighed. No. 3 is likewise precipitated and digested with potassium iodide until entirely converted into silver iodide, then weighed. In Crookes' example the iodine is replaced by bromine and the bromine by chlorine. In the first case the weights increase, and in the second they decrease.

Now suppose we try to derive a formula for each of these cases, beginning with Woodward's and using the same data as before, also  $\text{Ag} = 108$ ,  $\text{I} = 127$ ,  $\text{Br} = 80$ .

Woodward's Chemical Arithmetic.

Mixture of silver iodide, silver chloride and silver bromide.

$$\text{AgI} + \text{AgBr} + \text{AgCl} = W,$$

$$\text{AgI} + \text{AgBr} + \text{AgBr} = W',$$

$$\text{AgI} + \text{AgI} + \text{AgI} = W''.$$

Let  $x = \text{AgCl}$ ,  $a =$  molecular weight.

$$y = \text{AgBr}, b = \quad \quad \quad "$$

$$z = \text{AgI}, c = \quad \quad \quad "$$

$$x + y + z = W,$$

$$\frac{b}{a}x + y + z = W',$$

$$\frac{c}{a}x + \frac{c}{b}y + z = W'',$$

$$x = \frac{a(W' - W)}{b - a},$$

$$y = \frac{b(W'' - W')}{c - b} - \frac{b(W' - W)}{b - a},$$

$$z = W' - \frac{b(W'' - W')}{c - b}.$$

Crookes', same data :

$$\text{AgI} + \text{AgBr} + \text{AgCl} = W,$$

$$\text{AgBr} + \text{AgBr} + \text{AgCl} = W',$$

$$\text{AgCl} + \text{AgCl} + \text{AgCl} = W'',$$

$$x + y + z = W,$$

$$x + y + \frac{b}{c}z = W',$$

$$x + \frac{a}{b}y + \frac{a}{c}z = W'',$$

$$z = \frac{c(W - W')}{c - b},$$

$$y = \frac{b(W - W'')}{b - a} - \frac{b(W - W')}{c - b},$$

$$x = W' - \frac{b(W' - W'')}{b - a}.$$

#### FIRST METHOD.

Woodward's Example :

$$W = 27.19, W' = 30.87, W'' = 36.83, a = 143.45, b = 188, c = 235.$$

$$x = \frac{143.45 \times 3.68}{44.55} = 11.8495 \text{ AgCl} = 2.9282 \text{ Cl}$$

$$y = \frac{188 \times 5.96}{47} - \frac{188 \times 3.68}{44.55} = 8.3105 \text{ AgBr} = 3.5363 \text{ Br},$$

$$z = 30.87 - \frac{5.96 \times 188}{47} = 7.03 \text{ AgI} = 3.799 \text{ I}.$$

Crookes' Example :

$$W = 15.57, W' = 14.69, \text{ and } W'' = 12.20,$$

$$z = \frac{235 \times 0.88}{47} = 4.4 \text{ AgI},$$

$$y = \frac{188 \times 2.49}{44.55} - \frac{188 \times 0.88}{47} = 6.9877 \text{ AgBr},$$

$$x = 14.69 - \frac{188 \times 2.49}{44.55} = 4.1823 \text{ AgCl}.$$

#### SECOND METHOD.

Woodward's Example :

$$\text{AgCl} + \text{AgBr} + \text{AgI} = 27.19,$$

$$\text{AgBr} + \text{AgBr} + \text{AgI} = 30.87,$$

$$\text{AgI} + \text{AgI} + \text{AgI} = 36.83,$$

$$30.87 - 27.19 = 3.68,$$

$$44.55 : 3.68 = 143.45 : x = 11.8495 \text{ AgCl}.$$

$$\text{Now } 11.8495 \text{ AgCl} = 15.5295 \text{ AgBr} = 19.41187 \text{ AgI},$$

$$27.19 - 11.8495 = 15.3405,$$

$$36.83 - 19.41187 = 17.41813.$$

$$\text{Therefore } \text{AgBr} + \text{AgI} = 15.3405,$$

$$\text{AgI} + \text{AgI} = 17.41813,$$

$$17.41813 - 15.3405 = 2.07763,$$

$$47 : 2.07763 = 188 : x = 8.3105 \text{ AgBr}.$$

Adding the AgCl and AgBr thus found and subtracting their sum from 27.19, we get AgI = 7.03.

Comparison of results :

	Woodward.	First method.	Second method.
Cl .....	2.92	2.9283	2.9283
Br .....	3.51	3.5363	3.5363
I .....	3.69	3.799	3.799

Crookes' Example :

$$\begin{aligned}\text{AgCl} + \text{AgBr} + \text{AgI} &= 15.57, \\ \text{AgCl} + \text{AgBr} + \text{AgBr} &= 14.69, \\ \text{AgCl} + \text{AgCl} + \text{AgCl} &= 12.20, \\ 15.57 - 14.69 &= 0.88, \\ 47 : 0.88 &= 235 : x = 4.4 \text{ AgI.}\end{aligned}$$

$$\begin{aligned}\text{Now } 4.4 \text{ AgI} &= 3.52 \text{ AgBr} = 2.68586 \text{ AgCl,} \\ 15.57 - 4.4 &= 11.17, \\ 12.20 - 2.68586 &= 9.51414.\end{aligned}$$

$$\begin{aligned}\text{Therefore } \text{AgCl} + \text{AgBr} &= 11.17, \\ \text{AgCl} + \text{AgCl} &= 9.51414, \\ 11.17 - 9.51414 &= 1.65586, \\ 44.55 : 1.65586 &= 188 : x = 6.9877 \text{ AgBr.}\end{aligned}$$

Adding the AgI and AgBr thus found and subtracting their sum from 15.57, we get 4.1823 AgCl.

Comparison of results :

	Crookes.	First method.	Second method.
AgI.....	4.4	4.4	4.4
AgBr .....	6.998	6.9877	6.9877
AgCl.....	4.172	4.1823	4.1823

It will readily be seen that the first method requires less work than the second, and has the advantage of giving any of the three without the necessity of finding the others.

No originality is claimed for the foregoing, but the matter has been put in such a shape that it may be applied to any case, and any atomic weights may be used, thus making its application universal. In special cases it may be condensed by finding the factors by which to multiply the weights directly instead of multiplying by one number and dividing by another, but it was thought best to give the entire work as a help to those not conversant with algebra.

The writer would like to impress upon chemists the importance of giving the atomic weights and factors used in all calculations, so that their figures may be checked and errors avoided. As the atomic weights vary, important work may be recalculated and thus retain its value.



## NOTE ON THE MICROSCOPIC DETECTION OF BEEF FAT IN LARD.<sup>1</sup>

By THOMAS S. GLADDING.

Received January 3, 1896.

IN the preparation of crystals of lard and beef stearin for microscopic examination, I find the following method gives excellent results, the crystals being of good size and of distinctive form. Dissolve five cc. of melted lard in a mixture of ten cc. absolute alcohol and five cc. ether, in a small Erlenmeyer flask, heating gently if necessary. Place a plug of cotton in the mouth of the flask and allow to stand in a cool place for about half an hour. The stearin crystallizes out, the olein remaining in solution. Filter rapidly through a paper wet with alcohol, using a filter pump, and wash crystals and paper once with the above alcohol-ether mixture (10-5). Let the crystals dry in the air and remove them from the paper to the flask. Dissolve in twenty-five cc. of ether, replace the cotton plug, and place the flask in a slanting position in a large beaker (about one liter) nearly full of water. Keep this in a cool place over night. The ether evaporates very slowly and the crystals of stearin are gradually formed in the solution, the large quantity of water surrounding the ether solution guarding against any sudden change of temperature. For valuable plates giving characteristic forms of lard stearin crystals and beef stearin crystals reference is made to Bulletin No. 13, Part IV., Division of Chemistry, U. S. Department of Agriculture.

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### NOTES.

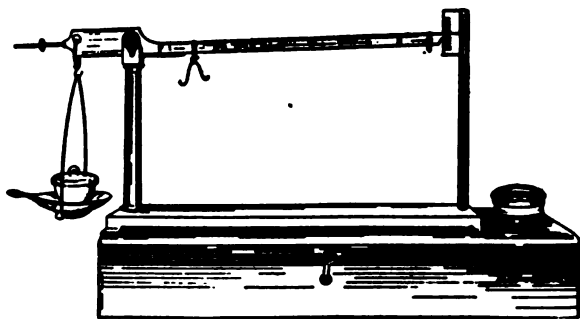
*The Estimation of Levulose in Honey.*—Through my negligence, I failed to call attention, on page 81 of the January number, to the optical method described by Allen, Commercial Organic Analysis, Vol. I, p. 291, relating to the estimation of levulose by changes in the specific rotatory power due to variations of temperature.

H. W. WILBY.

*A New Balance for First Year's Work in General Chemistry.*  
—The little balance shown in the cut was designed for the use

<sup>1</sup> Read at the Cleveland meeting, December 31, 1895.

of my students in their first year's laboratory practice, and has served its purpose so well in two large classes that I venture to call attention to it in the hope that others may find in



it a satisfactory solution of the balance problem in their schemes of beginners' laboratory work.

It is simple, efficient, and not expensive. The posts and beam are of lacquered brass; the base of iron. The length of the beam is twelve inches. The riders are of three weights, equivalent, when at the first division of the long arm, to 1.000, 0.100 and 0.010 gram respectively in the pan. Thus, in the cut, the weight of the crucible is 12.230 grams. The balance is sensitive to 0.010 with a load of 30.000 grams, and to 0.005 gram with a smaller load. Adjustment to zero before weighing is effected by means of a nut at the end of the short arm. It may be obtained of Messrs. Richards & Co., of New York.

JOHN TAPPAN STODDARD.

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### NEW BOOKS.

- ANALYTICAL CHEMISTRY. BY N. MENSCHUTKIN, PROFESSOR IN THE UNIVERSITY OF ST. PETERSBURG. Translated from the Third German Edition, under the Supervision of the Author, by James Locke. London and New York: Macmillan & Co. 512 pp. Price \$4.00.

Although the plan of treating the whole subject of analytical chemistry, qualitative and quantitative, in one volume has obvious merits, it is nevertheless something of a novelty, in this country at least, and on this and many other accounts this translation of Professor Menschutkin's work is very welcome.

It is not a book that can be used to the best advantage without good accompanying and supplementary instruction, and this is not because it is incomplete or unduly concise, but because the ideals and aims of the author are high ones, and the teacher is constantly needed to read between the lines. Principles are dealt with from the very first to the last and the *rationale* of the method is the point on which stress is laid. In the first part of the preface the author sets forth briefly his views as to the value of analytical work in a course of chemical study. His recommendation that it be not taken up too early is especially to be commended, as is also the plan of laying great stress upon the development of methods by the student himself, a practice altogether too uncommon.

The first 280 odd pages of the book deal with qualitative analysis. In its treatment of this difficult subject it differs markedly from the majority of treatises. There are no "tables" or "schemes." Each group of metals is first carefully studied with reference to its distinguishing group characteristics. Afterward the special properties and reactions of the individual members are taken up, and finally the analytical process deduced from the results. The plan of frequently giving solubilities quantitatively is a very helpful one. There are a few curious mistakes; for example, it is stated on p. 32 that potash alum is *less soluble* than the cesium and rubidium alums. The chromium bead is spoken of as *blue* instead of green (p. 70). This is evidently a slip of the pen, as the color is correctly given a few lines further on. Again on p. 126, in describing the analysis of columbite and tantalite, the mixture of oxides obtained by fusing the mineral with acid potassium sulphate and boiling out with water is said to be treated with ammonium *sulphite*, instead of *sulphide*. This, however, appears to be a misprint, as shown by the context. The word oxide is frequently used where hydroxide is meant.

The remaining 230 pages are devoted to quantitative analysis. This part of the book is treated in three sections. I. Gravimetric Analysis. II. Volumetric Analysis. III. Organic Analysis. In the first section the metals and metalloids are dealt with according to the following general plan: First the methods

are given for determining each individual of the group, then the methods for separating the different members of the group from each other. This is a better plan than the more common one of giving all the determinations first and afterwards all the separations.

The descriptions and directions are decidedly concise, but sufficient for the needs of fairly advanced students. Beginners will need and should in any case have considerable supplementary instruction. The non metals are treated according to the same general plan. A chapter of "operations and examples" follows, which might perhaps have been put with more profit at the beginning instead of at the end of the section.

Volumetric analysis is taken up according to the same plan as pervades the whole work. One very commendable thing about this and other parts of the book is that the student is not bewildered by a multitude of methods, but is simply made acquainted with such as have earned their right to existence. The section devoted to organic analysis is valuable and complete.

The translation is fully up to the average of such work. It reads for the most part smoothly and at least does not require retranslation into English, which is more than can be said of some recent efforts in this line.

JOSEPH TORREY, JR.

ON THE DENSITIES OF OXYGEN AND HYDROGEN, AND ON THE RATIO OF THEIR ATOMIC WEIGHTS. BY EDWARD W. MORLEY. 1895: Smithsonian Contributions to Knowledge. 4'. Forty cuts. xii., 117 pp. Price, \$1.00.

The ratio between oxygen and hydrogen is, to speak figuratively, the base-line upon which our entire system of atomic weights depends. But few of the other elements can be readily compared with hydrogen directly; practically all of them are referred to hydrogen through the intervention of oxygen; and so the atomic weight of the latter needs to be known with the utmost accuracy. A small error here becomes cumulative when introduced into the computation of higher values, and in the case of uranium it is multiplied to fifteen times its original magnitude.

Ten years ago the atomic weight of oxygen seemed to be pretty well known, and stood very nearly at 15.96. This, how-

ever, was near enough to the round number 16 to suggest that the difference might be due to error, and therefore reinvestigation began. First came Cooke and Richards, then Keiser, Noyes, Rayleigh, Dittmar and Henderson, and Leduc. Of these, Keiser alone approximated to the old value, finding  $O = 15.95$ . All of the others obtained results ranging from 15.866 to 15.897, with an outstanding uncertainty still larger than could long be tolerated. This uncertainty, thanks to Professor Morley, is now thrown into the third or fourth decimal place, and need no longer be troublesome.

The first and second divisions of Morley's monograph relate to the densities of the two gases, and are most elaborate in their details. Every precaution was taken to insure the purity of the material used, the methods of manipulation were varied, and every conceivable source of error seems to have been foreseen and guarded against.

For oxygen, three series of determinations are given. In the first series, the pressure and temperature of the gas to be weighed were determined by mercurial thermometers and a manobarmeter. In the second series, pressure and temperature were not observed for each experiment, but were made equal to the temperature and pressure of a standard volume of hydrogen, comparison being made by means of a differential manometer. In the third series the temperature was that of melting ice, and pressure alone was observed. For the weight of one liter of oxygen, at  $0^\circ$ , 760 mm., at sea level and in latitude  $45^\circ$ , the three series give as follows, in grams:

Series 1,	9 experiments,	$1.42879 \pm 0.000034$
"	2, 15	" $1.42887 \pm 0.000048$
"	3, 17	" $1.42917 \pm 0.000048$

On experimental grounds, Morley regards the third series as the best, and assigns it double weight. On this basis the general mean becomes

$$1.42900 \pm 0.000034.$$

The oxygen used was prepared partly from potassium chlorate, and partly by the electrolysis of dilute sulphuric acid.

For hydrogen, five series of determinations were made. In the first, the manipulations were like those of the first oxygen

series, with which it was strictly parallel. In the second, the weighing globes were surrounded by melting ice, and pressure was measured with a siphon barometer. In the third series the hydrogen was weighed, not in the globes where its pressure, temperature, and volume were taken, but before its introduction into them. Globes having a joint capacity of forty-two liters were connected together, for this series, and the hydrogen was weighed in palladium, of which 600 grams were used. The fourth and fifth series resembled the third. The hydrogen used was electrolytic. The results are subjoined, for the weight of one liter of hydrogen, in grams :

Series 1.	15 experiments,	$0.089938 \pm 0.000007$
"	2, 19	" $0.089970 \pm 0.000011$
"	3, 8	" $0.089886 \pm 0.000049$
"	4, 6	" $0.089880 \pm 0.000088$
"	5, 11	" $0.089866 \pm 0.000034$

In series 1 and 2, which Morley rejects, the hydrogen may have been contaminated by traces of mercurial vapor. In the remaining series that impurity was not present in the weighing of the gas, and exerts no influence upon the final result. Furthermore, in these series, stop-cocks were not used, and the connections were made by fusing the glass tubes into an unbroken continuity. The mean of series 4, 5, and 6 is

$$0.089873 \pm 0.000027,$$

and this is undoubtedly the best value yet found for the weight of a liter of hydrogen. Dividing this into the weight of oxygen, we have as the ratio of densities,

$$O = 15.9002.$$

In order to derive from this value the atomic weight of oxygen, the volumetric composition of water must be known. This subject forms the third part of Morley's memoir. He decomposed water by electrolysis, determined the density of the electrolytic mixed gases, and from that calculated the datum sought. The result is that in water, hydrogen and oxygen are combined in the ratio by volume of

$$2.00269 : 1.$$

Applying this ratio to the correction of the density ratio, we have

$$O = 15.879,$$

for the atomic weight of oxygen as given by the density method.

In the fourth part of the memoir Morley describes his gravimetric syntheses of water, which are the first really complete syntheses yet recorded. That is, nothing is taken by difference; hydrogen was weighed, oxygen was weighed, and the water formed was weighed, and all directly. By weighing the hydrogen in palladium, over three and eight-tenths grams could be taken in one experiment, a quantity which would be unmanageable in any attempt to weigh it in globes. Globes, however, were used for weighing the heavier oxygen; and the two gases were caused to combine by sparking in a suitable combustion apparatus. After combustion was complete, the apparatus containing the water was weighed, and the residual excess of gases left unburned was analyzed. The use of stop-cocks, in transferring the gases to the combustion apparatus, was completely avoided. Errors due to leakages, therefore, did not occur.

In all, twelve syntheses were made. Each one gives two values for the atomic weight of oxygen, except in one case, when the apparatus was broken. One value is derived from the weights of hydrogen and oxygen, the other from the weights of hydrogen and water. They are as follows:

H : O.	H : H <sub>2</sub> O.
15.878	15.877
15.881	15.878
15.878	15.873
15.880	lost
15.877	15.881
15.877	15.876
15.877	15.875
15.878	15.879
15.879	15.881
15.881	15.883
15.881	15.883
15.882	15.878
Mean, 15.8792	15.8785

The average of these two means is 15.87885, a result practically identical with that derived from the gaseous densities. The value, 15.879, then, is to be taken as the nearest approximation to the true atomic weight of oxygen, and this, for ordinary purposes, may be rounded off to 15.88.

It is hard to express an opinion concerning this great investigation, without seeming to be extravagant. In thoroughness, foresight, and manipulative skill it stands in the very front rank of chemical investigations, and on the same plane with the classical researches of Stas. In short, it is doubtful whether any better work of its kind has ever been published, and it has very few peers. To fully appreciate the memoir it must be studied in detail and at first hand; even Morley's own abstracts in various chemical journals fail to give an adequate impression of the magnitude of his achievement. The paper may at once take its place among "the classics of the exact sciences."

F. W. CLARKE.

### BOOKS RECEIVED.

Bulletin No. 41. Agr. Expt. Sta. Univ. of Minn. SOILS. Minneapolis, Minn. 1895, 79 pp. (1). The Essential Elements of Soil Fertility. (2). Humus as a Factor of Soil Fertility. (3). The Chemical and Mechanical Analyses of Soils. (4). The Action of Organic and Mineral Acids upon Soils. (5). Comparison of Different Methods of Farming upon the Conservation of Soil Fertility.

The Educational Value of Engineering studies. An address delivered on Founder's Day, Oct. 10, 1892, by Thomas M. Drown, LL.D. Lehigh University, Bethlehem, Pa. 1895. 30 pp.

The Chemist's Compendium. Compiled by C. J. S. Thompson. New York: Macmillan & Co. 1896. viii, 230 pp. Price \$1.00.

Practical Inorganic Chemistry. By G. S. Turpin, M. A., D. Sc., London and New York: Macmillan & Co., 1895. viii, 156 pp. Price 60 cents.

Bulletin No. 39. Analysis of Commercial Fertilizers. Baton Rouge: Agr. Expt. Sta. of La. 22 pp.

Bulletin of the Chemical Society of Washington, No. 9. Washington: The Society. 1895. 71 pp.

Lecture Notes on Theoretical Chemistry. By Ferdinand G. Weichmann, Ph. D. New York: John Wiley & Sons. 1895. xvii, 288 pp. Price \$3.00.

Chemistry for Engineers and Manufacturers. By Bertram Blount, F. I. C., F. C. S. and A. G. Bloxam, F. I. C., F. C. S. Vol. I. Chemistry of Engineering, Building and Metallurgy. Philadelphia: J. B. Lippincott Co. x, 244 pp. Price \$3.50.



# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### THIRD ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED DURING 1895.<sup>1</sup>

BY F. W. CLARKE.

Received January 3, 1896.

*To the Members of the American Chemical Society :*

YOUR committee upon atomic weights respectfully submits the following report, summarizing the work done in this branch of chemistry during 1895, a year which may be well called eventful in the history of the science. Two new elements, argon and helium, have been made known to the world, and from the most unexpected sources ; the collective works of Stas have been published by the Belgian Academy, as a monument to his memory ; Prof. Morley's great research upon oxygen is at last finished ; and a goodly number of other important determinations have appeared. Incidentally, but pertinently, I may also call attention to the Marignac memorial lecture by Cleve,<sup>2</sup> in which the atomic weight researches of the former chemist are well outlined ; and to the extraordinary number of papers upon the periodic law, which have been called out by the discovery of argon and helium. These papers fall outside the scope of this report, and they are numerous enough to almost warrant a bibliography of their own.

*The H: O ratio.*—Prof. Morley's work upon this fundamental constant has been published in full by the Smithsonian Insti-

<sup>1</sup> Read at the Cleveland Meeting, December 31, 1895.

<sup>2</sup> *J. Chem. Soc.*, June, 1895.

tute,<sup>1</sup> and divides itself naturally into four parts : First, the density of oxygen ; second, that of hydrogen ; third, the volumetric composition of water ; and fourth, its gravimetric synthesis.

For the density of oxygen, or rather the weight of one liter at 0°, 760 mm., at sea level and in latitude 45°, three sets of measurements are given, with the following mean values in grams :

Series 1.....	1.42879 ± 0.000034
" 2.....	1.42887 ± 0.000048
" 3.....	1.42917 ± 0.000048

As the third series, on experimental grounds, is regarded by Morley as the best, he assigns it double weight, and on this basis the general mean of all three becomes

$$1.42900 \pm 0.000034.$$

For the weight of a liter of hydrogen, under similar standard conditions, five series of determinations are given, as follows :

Series 1.....	0.089938
" 2.....	0.089970
" 3.....	0.089886 ± 0.0000049
" 4.....	0.089880 ± 0.0000088
" 5.....	0.089866 ± 0.0000034

The hydrogen of the first and second series was probably contaminated by traces of mercurial vapor, and these results are therefore rejected by Morley. For the third, fourth and fifth series the electrolytic gas was occluded in palladium and transferred to the measuring globes without the intervention of stop-cocks ; thus avoiding contact with mercury and leakages of external air. Their general mean is

$$0.089873 \pm 0.0000027.$$

Dividing the weight found for oxygen by this value for hydrogen the ratio becomes

$$15.9002.$$

For the volumetric ratio O : 2H, Morley finds the value

<sup>1</sup> "On the Density of Oxygen and Hydrogen, and on the Ratio of their Atomic Weights." By Edward W. Morley. Smithsonian Contributions to Knowledge, 1895. 4to. 81 + 117 pp. 40 cents. Abstract in *Am. Chem. J.*, 17, 267, (gravimetric) ; and *Ztschr. phys. Chem.*, 17, 87, (gaseous densities) ; also note in *Am. Chem. J.*, 17, 396.

1: 2.00269. Applying this as a correction to the density ratio, we have for the atomic weight of oxygen

$$O = 15.879.$$

In his synthesis of water Morley differs from all of his predecessors in that he weighed both constituents separately, and also the water formed. In other words, his syntheses are complete, and take nothing for granted. The weights in grams, are as follows :

	O used.	H used.	Water found.
1 .....	25.9176	3.2645	29.1788
2 .....	25.8531	3.2559	29.1052
3 .....	30.3210	3.8193	34.1389
4 .....	30.5294	3.8450	Lost.
5 .....	30.4700	3.8382	34.3151
6 .....	30.5818	3.8523	34.4327
7 .....	30.4013	3.8297	34.2284
8 .....	30.3966	3.8286	34.2261
9 .....	30.3497	3.8225	34.1742
10 .....	30.3479	3.8220	34.1743
11 .....	29.8865	3.7637	33.6540
12 .....	30.3429	3.8211	34.1559

From these data, two sets of values for the atomic weight of oxygen are derivable ; one from the ratio H : O, the other from the ratio H : H<sub>2</sub>O. These sets are subjoined.

	H : O.	H : H <sub>2</sub> O.
1 .....	15.878	15.877
2 .....	15.881	15.878
3 .....	15.878	15.873
4 .....	15.880	.....
5 .....	15.877	15.881
6 .....	15.877	15.876
7 .....	15.877	15.875
8 .....	15.878	15.879
9 .....	15.879	15.881
10 .....	15.881	15.883
11 .....	15.881	15.883
12 .....	15.882	15.878
Mean .....	15.8792	15.8785

From the density work the value found was 15.879, and the mean of this with the two synthetic results is

$$O = 15.8789.$$

Hence, for all practical purposes the atomic weight of oxygen may be put at 15.88, with an uncertainty of less than one unit in the second decimal.

It is impracticable, in a report of this kind, to go into the details of so elaborate an investigation as this of Morley's, and a bare statement of results must suffice. The research, however, is one of the most perfect of its kind, every source of error having been considered and guarded against, and it will doubtless take its place in chemical literature as a classic. Independently of its main purpose, the book is almost a manual on the art of weighing and measuring gases, and no experimenter who engages upon work of that kind can afford to overlook it.

More recently still, a new determination of the atomic weight of oxygen has been published by Julius Thomsen,<sup>1</sup> whose method is quite novel. First, aluminum, in weighed quantities, was dissolved in caustic potash solution. In one set of experiments the apparatus was so constructed that the hydrogen evolved was dried and then expelled. The loss of weight of the apparatus gave the weight of the hydrogen so liberated. In the second set of experiments the hydrogen passed into a combustion chamber in which it was burned with oxygen, the water being retained. The increase in weight of this apparatus gave the weight of oxygen so taken up. The two series, reduced to the standard of a unit weight of aluminum, gave the ratio between oxygen and hydrogen.

The results of the two series, reduced to a vacuum and stated as ratios, are as follows :

First, $\frac{\text{Weight of H.}}{\text{Weight of Al.}}$	Second, $\frac{\text{Weight of O.}}{\text{Weight of Al.}}$
First.	Second.
0.11180	0.88788
0.11175	0.88799
0.11194	0.88774
0.11205	0.88779
0.11189	0.88785
0.11200	0.88789
0.11194	0.88798
0.11175	0.88787

<sup>1</sup> *Ztsch. anorg. Chem.*, 11, 14.

First.	Second.
0.11190	0.88773
0.11182	0.88798
0.11204	0.88785
0.11202	
0.11204	0.88787 $\pm$ 0.000018
0.11179	
0.11178	
0.11202	
0.11188	
0.11186	
0.11185	
0.11190	
0.11187	
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0.11190 $\pm$ 0.000015.	

Dividing the mean of the second column by the mean of the first, we have for the equivalent of oxygen:

$$\frac{0.88787 \pm 0.000018}{0.11190 \pm 0.000015} = 7.9345 \pm 0.0011.$$

$$\text{Hence, O} = 15.8690 \pm 0.0022.$$

The details of the investigation are somewhat complicated, and involve various corrections which need not be considered here. The result as stated, includes all corrections and is evidently good. The ratios, however, cannot be reversed and used for measuring the atomic weight of aluminum, because the metal employed was not absolutely pure.

*The Stas Memorial.*—As a monument to the memory of the late Jean Servias Stas, more appropriate than statue or column of stone, the Belgian Academy has published his collected works in three superb quarto volumes.<sup>1</sup> All of his great investigations are here gathered together, and in the third volume, entitled "Oeuvres Posthumes," some hitherto unpublished data are given for the important ratio between potassium chloride and silver. These data are represented by two series: one made with a uniform sample of silver, and chloride from various sources; the other with constant chloride, but with silver of diverse origin; the aim being to establish experimentally the fixed character of each substance. The first series is complete;

<sup>1</sup> Jean Servias Stas. *Oeuvres Complètes*. Edited by W. Spring. Bruxelles, 1894.

of the second series only one experiment was found recorded among Stas' papers.

The quantity of potassium chloride equivalent to 100 parts of silver was found to be as follows :

	69.1227
	69.1236
	69.1234
	69.1244
	69.1235
	69.1228
	69.1222
	69.1211
	69.1219
	69.1249
	69.1238
	69.1225
	69.1211
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Mean of first series	69.1229
Second series	69.1240

These results give an effective confirmation to Stas' determinations of 1882.

**Cobalt.**—The atomic weight of cobalt has been redetermined by Thiele.<sup>1</sup> First, carefully purified oxide of cobalt, CoO, was reduced in hydrogen. The weight and results are as follows :

Residual Co.	Loss of O.	Atomic weight of Co
0.90068	0.24429	58.843
0.79159	0.21445	58.912
1.31558	0.35716	58.788
		<hr/>
	Mean	58.848

Reduced to vacuum standards this becomes

$$\text{Co} = 58.826,$$

when O = 15.96.

In a second method metallic cobalt was dissolved in hydrochloric acid, and the solution evaporated to dryness with special precautions against dust. The chloride thus obtained was then dried at 150° in a stream of pure gaseous hydrochloric acid, so that basic salts could not be formed. From the weight of cobalt

<sup>1</sup> "Die Atomgewichtsbestimmung des Kobalts." A doctoral dissertation. Basel, 1892.

and of cobalt chloride the ratio  $\text{Co}:\text{Cl}_2$  is determined. The chlorine was afterwards re-estimated as silver chloride, giving the ratio  $\text{Co} : 2\text{AgCl}$ . The weights are subjoined :

Co taken.	Cl taken up.	AgCl.
0.7010	0.8453	.....
0.3138	0.3793	.....
0.2949	0.3562	1.4340
0.4691	0.5657	2.2812
0.5818	0.7026	2.8303
0.5763	0.6947	.....
0.5096	0.6142	2.4813

Hence, with  $\text{Cl} = 35.37$ , and  $\text{Ag} = 107.66$ ,  $\text{Co} =$

$\text{Co}:\text{Cl}_2$ .	$\text{Co} : 2\text{AgCl}$ .
58.66	.....
58.52	.....
58.57	58.828
58.66	58.825
58.58	58.803
58.68	.....
58.69	58.750

Mean 58.64

Mean, 58.801

The second column is subject to a small correction for dissolved silver chloride, which reduces the mean to  $\text{Co} = 58.770$ . Reduced to a vacuum this becomes 58.765, and the value from the  $\text{Co}:\text{Cl}_2$  ratio becomes 58.61. Thiele regards  $\text{Co} = 58.765$  as the most probable value to be derived from his experiments. This becomes

With $\text{O} = 16$ ,	$\text{Co} = 58.912$
" $\text{O} = 15.88$ ,	$\text{Co} = 58.470$ .

In my report for 1894 I gave Winkler's work on cobalt and nickel, which involved their ratios to iodine. In a supplementary paper Winkler<sup>1</sup> gives some similar experiments with iron, intended to show that errors due to metallic occlusion of hydrogen are absent from his determinations. He succeeds in proving that such errors, if they exist, must be very small. Thiele also considered their possibility, and guarded against them in the preparation of his cobalt.

*Zinc*.—Atomic weights redetermined by Richards and Rogers,<sup>2</sup>

<sup>1</sup> *Ztschr. anorg. Chem.*, 3, 291.

<sup>2</sup> *Ztschr. anorg. Chem.*, 10, 1. Calculations made with  $\text{O} = 16$ ,  $\text{Ag} = 107.93$ , and  $\text{Br} = 79.955$ .

who used the bromide method. Zinc bromide, carefully purified, was treated gravimetrically with standard silver solution. The weights and results are subjoined :

First,  $\text{ZnBr}_2 : 2\text{AgBr}$ .

$\text{ZnBr}_2$ .	$\text{AgBr}$ .	Atomic weight of Zn.
1.69616	2.82805	65.469
1.98198	3.30450	65.470
1.70920	2.84549	65.487
2.35079	3.91941	65.470
2.66078	4.43751	65.400
		<hr/>
		Mean, 65.459

## Second, same ratio.

$\text{ZnBr}_2$ .	$\text{AgBr}$ .	Atomic weight of Zn.
2.33882	3.90067	65.400
1.97142	3.28742	65.434
2.14985	3.58539	65.402
2.00966	3.35074	65.463
		<hr/>
		Mean, 65.425

Third,  $\text{ZnBr}_2 : \text{Ag}_2$ .

$\text{ZnBr}_2$ .	$\text{Ag}_2$ .	Atomic weight of Zn.
2.33882	2.24063	65.409
1.97142	1.88837	65.444
2.14985	2.05971	65.396
2.00966	1.92476	65.472
		<hr/>
		Mean, 65.430

Two additional series of data are given by Richards alone, as follows :

First,  $\text{ZnBr}_2 : \text{Ag}_2$ .

$\text{ZnBr}_2$ .	$\text{Ag}_2$ .	Atomic weight of Zn.
6.23833	5.9766	65.403
5.26449	5.0436	65.404
9.36283	8.9702	65.392
		<hr/>
		Mean, 65.402

Second,  $\text{ZnBr}_2 : 2\text{AgBr}$ .

$\text{ZnBr}_2$ .	$\text{AgBr}$ .	Atomic weight of Zn.
2.65847	4.43358	65.410
2.30939	3.85149	65.404
5.26449	8.77992	65.404
		<hr/>
		Mean, 65.406



The final mean adopted by Richards is 65.404. With O = 15.88 this becomes

$$\text{Zn} = 64.913.$$

*Cadmium*.—Mr. Bucher's paper,<sup>1</sup> as its title indicates, is a study of methods rather than a final determination of atomic weight; but the results recorded in it compare well with those reached by others. His starting point is metallic cadmium, purified by nine distillations *in vacuo*, and from this material, with pure reagents, his various preparations were made. Vacuum weights are given, and the antecedent values used in calculation are O, 16; S, 32.059; C, 12.003; Cl, 35.45; Br, 79.95; and Ag, 107.93.

First, cadmium oxalate, dried for fifty hours at 150°, was decomposed by heat, and so reduced to oxide. The variations are mainly attributed to imperfect dehydration of the oxalate.

Weights and results are as follows:

Oxalate.	Oxide.	Atomic weight of Cd.
1.97674	1.26474	111.74
1.94912	1.24682	111.83
1.97686	1.25886	111.85
1.87099	1.19675	111.81
1.37550	0.87994	111.86
1.33313	0.85308	111.96
1.94450	1.24452	112.02
2.01846	1.29210	112.09

Mean, 111.89

Second, cadmium oxalate was transformed to sulphide by heating in a stream of hydrogen sulphide. The data are:

Oxalate.	Sulphide.	Atomic weight of Cd.
2.56319	1.84716	112.25
2.18364	1.57341	112.19
2.11643	1.52462	112.03
3.13105	2.25582	112.12

Mean, 112.15

Third, cadmium chloride, dried at 300° in a stream of dry, gaseous hydrochloric acid, was precipitated by silver nitrate, and the silver chloride was collected with all necessary precautions. The weights and results are subjoined:

<sup>1</sup> "An examination of some methods employed in determining the atomic weight of cadmium." By John E. Bucher. Johns Hopkins University doctoral dissertation. Baltimore (Friedenwald), 1895.

CdCl <sub>2</sub> .	AgCl.	Atomic weight of Cd.
3.09183	4.83856	112.34
2.26100	3.53854	112.33
1.35729	2.12431	112.32
2.05582	3.21727	112.34
1.89774	2.97041	112.31
3.50367	5.48473	112.28
2.70292	4.23087	112.30
4.24276	6.63598	112.44
3.40200	5.32314	112.37
4.60659	7.20386	112.47
2.40832	3.76715	112.42
2.19144	3.42724	112.46
2.84628	4.45477	112.32
2.56748	4.01651	112.41
2.31003	3.61370	112.41
1.25008	1.95652	112.32
1.96015	3.06541	112.47
2.29787	3.59391	112.45
1.94227	3.03811	112.42
1.10976	1.73547	112.47
1.63080	2.55016	112.48

Mean, 112.39

Fourth, cadmium bromide was analyzed in much the same way as the chloride. The weights and results are as follows :

CdBr <sub>2</sub> .	AgBr.	Atomic weight of Cd.
4.39941	6.07204	112.35
3.18030	4.38831	112.42
3.60336	4.97150	112.45
4.04240	5.58062	112.29
3.60505	4.97519	112.38

Mean, 112.38

Fifth, cadmium sulphate was formed by synthesis from metallic cadmium. 1.15781 grams cadmium gave 2.14776 cadmium sulphate. Hence Cd = 112.35. As any impurity in the sulphate would tend to lower the atomic weight found, this is probably a minimum value.

Sixth, metallic cadmium was converted into oxide by solution in nitric acid and ignition of the nitrate. The ignition was performed in double crucibles, both porcelain in experiments 1 and 2, the inner one of platinum in the rest of the series. Weights and results as follows :

Cd.	CdO.	Atomic weight of Cd.
1.26142	1.44144	112.12
0.99785	1.40135	112.04
	Mean,	112.08
1.11321	1.27247	111.84
1.02412	1.17054	111.91
2.80966	3.21152	111.87
	Mean,	111.87

In this case additional experiments were made to discover the sources of error, leading to corrections which bring the results near to those found in the chloride and bromide series. Each of the methods is quite fully discussed, and the sources of error are noted. With  $O = 16$ , 112.39 seems to be a close approximation to the true atomic weight of cadmium.

*Molybdenum*.—Seubert and Pollard,<sup>1</sup> by two distinct methods, have redetermined the atomic weight of this element. First, molybdenum trioxide was dissolved, in weighed quantities, in a standard solution of caustic soda. The excess of soda was then measured by titration with standard sulphuric acid and lime water. In another set of experiments the volumetric value of the caustic soda had been estimated with standard hydrochloric acid, while the last compound had also been determined gravimetrically in terms of silver chloride. Hence the data, all considered together, give from their true end terms, the ratio  $MoO_3 : 2AgCl$ , although in a very indirect manner; and for this indirection the authors give good reasons. The weights and results, considering only the end terms, are as follows:

$MoO_3$ .	$AgCl$ .	Atomic weight of Mo.
3.6002	7.1709	95.734
3.5925	7.1569	95.708
3.7311	7.4304	95.757
3.8668	7.7011	95.749
3.9361	7.8407	95.720
3.8986	7.7649	95.740
3.9630	7.8941	95.723
3.9554	7.8806	95.694
3.9147	7.7999	95.686
3.8543	7.6767	95.740
3.9367	7.8437	95.688
	Mean,	95.722

<sup>1</sup> *Ztschr. anorg. Chem.*, 8, 434. Calculations on the basis of  $O = 15.96$ .

Reduced to vacuum standards this becomes  $\text{Mo} = 95.729$ . With  $\text{O} = 16$ ,  $\text{Mo} = 95.969$ ; and with  $\text{O} = 15.88$ ,  $\text{Mo} = 95.249$ .

Another series of determinations, in confirmation of the first, was made by the old method of reducing molybdenum trioxide in hydrogen. The weights and results are subjoined :

$\text{MoO}_3$ .	Mo.	Atomic weight of Mo.
1.8033	1.2021	95.736
1.7345	1.1564	95.777
3.9413	2.6275	95.756
1.5241	1.0160	95.741
4.0533	2.7027	95.813
Mean,		95.765

Reduced to vacuum,  $\text{Mo} = 95.735$ , a value very close to the other. When  $\text{O} = 16$ , the atomic weight of molybdenum is very near the even number 96.

*Tellurium*.—The determinations of atomic weight by Staudenmeier<sup>1</sup> all start out from telluric acid,  $\text{H}_2\text{TeO}_6 \cdot 2\text{H}_2\text{O}$ , which had been purified by repeated crystallization. Two essentially different methods were adopted. First, telluric acid was dehydrated, and reduced to  $\text{TeO}_2$  by heating. Secondly, telluric acid was reduced by heating in hydrogen to metallic tellurium, finely divided silver being mixed with the acid to retain the tellurium by preventing volatilization. In four experiments,  $\text{TeO}_2$  was reduced to  $\text{Te}$  in the same manner. The weights and results may be classified as follows, for convenience of comparison :

$\text{TeO}_2 : \text{Te}$ .

$\text{TeO}_2$ .	Loss on reduction.	Atomic weight of Te.
0.9171	0.1839	127.6
1.9721	0.3951	127.7
2.4115	0.4835	127.6
1.0172	0.2041	127.5

TELLURIC ACID :  $\text{TeO}_2$ .

Telluric acid.	Loss.	Atomic weight of Te.
1.7218	0.5260	127.2
2.8402	0.8676	127.1
4.0998	1.2528	127.1
3.0916	0.9450	127.05
1.1138	0.3405	127.0
4.9843	1.5236	127.05
4.6716	1.4278	127.1

<sup>1</sup> *Ztschr. anorg. Chem.*, 10, 189. Calculations based upon  $\text{O} = 16$  and  $\text{H} = 1.0032$ .

## TELLURIC ACID : Te.

Telluric acid.	Loss.	Atomic weight of Te.
1.2299	0.5471	127.3
1.0175	0.4526	127.3
2.5946	1.1549	127.2

There is a good discussion in the paper as to the possible causes of error in these determinations, and also concerning the place of tellurium in the periodic system. Staudenmeier upholds the homogeneity of tellurium as an element, as against the supposition that it is a mixture.

Some years ago Brauner, in an elaborate paper upon tellurium, sought to show that the ordinary element was a mixture of true tellurium with a higher homologue of atomic weight 214. He now<sup>1</sup> concludes that this is very improbable, and suggests that tellurium may contain a homologue of argon, of atomic weight 130. For this supposition no evidence is given apart from the abnormality of the atomic weight, which should fall below that of iodine.

*Yttrium.*—The atomic weight of this metal has been redetermined by Jones,<sup>2</sup> who starts out with material purified by Rowland's process, that is, by precipitation with potassium ferrocyanide. First, oxide was converted into sulphate; and secondly, sulphate was transformed to oxide by calcination. The weights and results were as follows:

## FIRST METHOD.

$Y_2O_3$ .	$Y_4(SO_4)_3$ .	Atomic weight of Y.
0.2415	0.4984	88.89
0.4112	0.8485	88.92
0.2238	0.4617	88.97
0.3334	0.6879	88.94
0.3408	0.7033	88.90
0.3418	0.7049	89.05
0.2810	0.5798	88.94
0.3718	0.7803	88.89
0.4379	0.9032	89.02
0.4798	0.9901	88.91

Mean, 88.94

<sup>1</sup> *J. Chem. Soc.*, 67, 549.

<sup>2</sup> *Am. Chem. J.*, 17, 154. Calculations made with O = 16, and S = 32.06.

## SECOND METHOD.

$Y_2(SO_4)_3$ .	$Y_2O_3$ .	Atomic weight of Y.
0.5906	0.2862	88.91
0.4918	0.2383	88.89
0.5579	0.2705	89.03
0.6430	0.3117	88.99
0.6953	0.3369	88.89
1.4192	0.6880	88.99
0.8307	0.4027	88.99
0.7980	0.3869	89.02
0.8538	0.4139	88.99
1.1890	0.5763	88.96
Mean,		88.97

These determinations are probably the best hitherto made, although they have been briefly criticized by Delafontaine,<sup>1</sup> who prefers the lower value obtained by himself,  $Y = 87.3$ . Delafontaine reaffirms the existence of phillipium, and regards gadolinium as identical with decipium. Jones,<sup>2</sup> in a brief rejoinder defends his own work, and urges that Delafontaine has failed to show wherein it is defective.

*The Cerite Earths.*—Papers upon this subject have been published during the year by Schutzenberger and by Brauner. In his first communication, Schuntzeberger<sup>3</sup> deals with cerium, which had been freed from lanthanum and "didymium" by fusion of the mixed nitrates with saltpeter. The yellowish-white cerium oxide was converted into cerium sulphate, which was dried at  $440^\circ$ . In this salt, with special precautions, the sulphuric acid was estimated by precipitation with barium chloride. One hundred parts of cerium sulphate gave 123.30 of barium sulphate. Hence,  $Ce = 139.45$ , according to Schutzenberger's calculations. Recomputing, with

$$O = 16, S = 32.07, \text{ and } Ba = 137.43.$$

$$Ce = 139.96.$$

In a second paper,<sup>4</sup> Schutzenberger describes the results obtained by the fractionation of cerium sulphate. Preparations were thus secured giving oxides of various colors, such as canary yellow, yellowish rose, reddish, and brownish red. These,

<sup>1</sup> *Chem. News*, 71, 243.

<sup>2</sup> *Chem. News*, 71, 305.

<sup>3</sup> *Compt. rend.*, 120, 663.

<sup>4</sup> *Compt. rend.*, 120, 962.

by the synthesis of the sulphates, the barium sulphate method, etc., gave varying values for cerium ranging from 135.7 up to 143.3. Schutzenberger concludes that the cerium sesquioxide from cerite contains small quantities of another earth of lower atomic weight. In a third paper<sup>1</sup> he continues the investigation with the other cerite earths. For the didymiums he finds a range in atomic weight from 137.5 to 143.5, approximately.

Brauner's paper<sup>2</sup> is partly a reclamation of priority over Schutzenberger, and partly a preliminary statement of new results. In his earlier work he found that cerium oxide was a mixture of two earths; one white, the other flesh color with a tinge of orange, and atomic weights for the contained metal of 140.2 and 145.72, respectively. In his later researches Brauner fractionates his material by several methods. One constituent obtained from cerium oxide is a dark salmon-colored earth, the oxide of a metal which he calls "meta-cerium." The other constituent he calls cerium. Pure cerium oxalate by Gibbs' permanganate method gave 29.506 and 29.503 per cent. of cerium sesquioxide with 46.934 per cent. of cerium dioxide. Hence,  $Ce = 139.91$ , or, with a slight correction,  $Ce = 140.01$ . This is not far from Schutzenberger's value.

*Helium and Argon.*—The true atomic weights of these remarkable gases are still in doubt, and so far can only be inferred from their specific gravities. For argon, the discoverers, Rayleigh and Ramsay,<sup>3</sup> give various determinations of density, ranging ( $H = 1$ ) from 19.48 to 20.6. The value 19.9 they regard as approximately correct.

For helium, Ramsay<sup>4</sup> gives the density 2.18, while Langlet<sup>5</sup> finds the somewhat lower value 2.00.

From one set of physical data, both gases appear to be monatomic, but from other considerations they are supposedly diatomic. Upon this question, controversy has been most active, and no final settlement has yet been reached. If diatomic, argon and helium have approximately the atomic weights, two

<sup>1</sup> *Compt. rend.*, 180, 1143.

<sup>2</sup> *Chem. News.*, 71, 283.

<sup>3</sup> *Phil. Trans.*, 186, 220-223.

<sup>4</sup> *J. Chem. Soc.*, 3, 684.

<sup>5</sup> *Ztschr. anorg. Chem.*, 10, 289.

and twenty, respectively; if monatomic, these values must be doubled. In either case, helium is an element lying between hydrogen and lithium; but argon is most difficult to classify. With the atomic weight 20, argon fills in the eighth column of the periodic system, between fluorine and sodium; but if it is 40, the position of the gas is anomalous. A slightly lower value would place it between chlorine and potassium, and again in the eighth column of Mendeleeff's table, but for the number 40 no opening can be found.

It must be noted that neither gas, so far, has been proved to be absolutely homogeneous; and it is quite possible that both may contain admixtures of other things. This consideration has been repeatedly urged by various writers. If argon is monatomic, a small impurity of greater density, say of an unknown element falling between bromine and rubidium, would account for the abnormality of its atomic weight, and tend towards the reduction of the latter. If the element is diatomic, its classification is easy enough on the basis of existing data. Its resemblances to nitrogen, as regards density, boiling point, difficulty of liquefaction, etc., lead me personally to favor the lower figure for its atomic weight, and the same considerations may apply to helium also. Until further evidence is furnished, therefore, I shall assume the values two and twenty as approximately true for the atomic weight of helium and argon.

*Carbon.*—Wanklyn,<sup>1</sup> on the basis of his investigations into the composition of hydrocarbons, reiterates his belief that the atomic weight of carbon is not 12, but 6. This question is one which falls rather outside the scope of this report and needs no further discussion here. If Wanklyn's contention is sustained, the value assigned to carbon in the table at the close of this paper, should be divided by two.

In the following table of atomic weights, the values are given according to both standards,  $H = 1$  and  $O = 16$ . Many of the figures are the results of new and complete recalculation from all available data, made in the preparation of a new edition of my "Recalculation of the Atomic Weights." This work is now well under way, and it will probably be completed during 1896:

<sup>1</sup> *Chem. News*, 72, 164. See also *Phil. Mag.*, August, 1895. Also the reports of this committee for 1893 and 1894.



	H = 1.	O = 16.
Aluminum .....	26.91	27.11
Antimony .....	119.52	120.43
Argon .....	?	?
Arsenic .....	74.52	75.09
Barium .....	136.40	137.43
Bismuth .....	206.54	208.11
Boron .....	10.86	10.95
Bromine .....	79.34	79.95
Cadmium .....	111.08	111.93
Cesium .....	131.89	132.89
Calcium .....	39.78	40.08
Carbon .....	11.92	12.01
Cerium .....	139.1	140.2
Chlorine .....	35.18	35.45
Chromium .....	51.74	52.14
Cobalt .....	58.49	58.93
Columbium .....	93.3	94.0
Copper .....	63.12	63.60
Erbium .....	165.0	166.3
Fluorine .....	18.89	19.03
Gadolinium .....	154.9	156.1
Gallium .....	68.5	69.0
Germanium .....	71.75	72.3
Glucinum .....	9.01	9.08
Gold .....	195.74	197.24
Helium .....	?	?
Hydrogen .....	1.00	1.008
Indium .....	112.8	113.7
Iodine .....	125.89	126.85
Iridium .....	191.66	193.12
Iron .....	55.60	56.02
Lanthanum .....	137.6	138.6
Lead .....	205.36	206.92
Lithium .....	6.97	7.03
Magnesium .....	24.11	24.29
Manganese .....	54.57	54.99
Mercury .....	198.5	200.0
Molybdenum .....	95.26	95.98
Neodymium .....	139.4	140.5
Nickel .....	58.24	58.69
Nitrogen .....	13.94	14.04
Osmium .....	189.55	190.99
Oxygen .....	15.879	16.00
Palladium .....	105.56	106.36
Phosphorus .....	30.79	31.02

Platinum .....	193.41	194.89
Potassium.....	38.82	39.11
Praseodymium .....	142.4	143.5
Rhodium .....	102.23	103.01
Rubidium.....	84.78	85.43
Ruthenium .....	100.91	101.68
Samarium .....	148.9	150.0
Scandium.....	43.7	44.0
Selenium .....	78.4	79.0
Silicon.....	28.18	28.40
Silver.....	107.11	107.92
Sodium .....	22.88	23.05
Strontium.....	86.95	87.61
Sulphur.....	31.83	32.07
Tantalum .....	181.2	182.6
Tellurium .....	126.1 ?	127.0 ?
Terbium .....	158.8	160.0
Thallium .....	202.60	204.15
Thorium .....	230.87	232.63
Thulium .....	169.4	170.7
Tin .....	118.15	119.05
Titanium .....	47.79	48.15
Tungsten .....	183.44	184.84
Uranium.....	237.77	239.59
Vanadium.....	50.99	51.38
Ytterbium .....	171.7	173.0
Yttrium .....	88.28	88.95
Zinc .....	64.91	65.41
Zirconium .....	89.9	90.6

### COMPOSITION OF WOOD GUM.

By S. W. JOHNSON.

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SINCE 1879, when Thomsen published his investigation of "Wood Gum," the writer has, from time to time, as opportunity offered, employed several of the chemists of the Connecticut Agricultural Experiment Station in work upon the alkali-soluble carbohydrates of maize cobs, birch wood and vegetable ivory. This work has necessarily been subject to frequent and prolonged interruptions, and for that reason the publication of conclusive results has been greatly delayed.

Wood gum, which is abundantly extracted from the wood of deciduous trees by cold, weak (two to ten per cent.) solutions of

sodium or potassium hydroxide, and thrown down therefrom by neutralization and by alcohol, has been analyzed by Thomsen, Koch, Schuppe and by Wheeler and Tollens.<sup>1</sup>

With exception of Schuppe, all these investigators obtained results on the whole agreeing fairly with the formula  $C_6H_{10}O_5$ .

Schuppe's analyses mostly gave higher figures for carbon and hydrogen.

*Xylan*.—When it was shown by Wheeler and Tollens that xylose, the sugar first described by Koch, and obtained by him, from the products of the hydrolysis of wood gum, has the formula  $C_6H_{10}O_5$ , it became extremely probable that the corresponding anhydride, now designated xylan, has the composition  $C_6H_8O_4$ .

Analyses made in this laboratory in 1885 demonstrated that the cobs of Indian corn yield to five or ten per cent. potassium hydroxide solution, a body, which, precipitated by alcohol, acidulated with hydrochloric acid, suitably washed and thoroughly dried, has in fact the composition proper to pure xylan.

In 1880 xylan was thus prepared under my direction by Dr. Jenkins, as follows: Ground maize cob was digested for twenty-four hours with frequent agitation in a mixture of one volume of concentrated ammonia with seven volumes of water, the residue was washed on filters to remove all ammonia and digested forty-eight hours with seven per cent. caustic soda solution. The filtered extract was mixed with twice its volume of ninety-three per cent. alcohol. The precipitate was washed until the washings were neutral to test papers, then was stirred up with dilute hydrochloric acid, again washed with dilute alcohol until neutral and thereupon was further treated with absolute alcohol and ether and dried over sulphuric acid. About twenty-five per cent. of white, easily powdered material were thus obtained, which answered to Thomsen's description of wood gum.

It was not made blue by iodine solution. Agitated with pure water at common temperatures for a considerable time, it was taken up to the extent of 0.14 per cent., giving a neutral solution. Boiled for six hours with water, a neutral solution resulted, which contained 0.44 per cent. of dissolved substance that very slightly reduced Fehling's solution. The solution in hot water was unaf-

<sup>1</sup>Ann. Chem. (Liebig) 284, 320.

fects by addition of normal lead acetate, but with basic lead acetate gave a heavy flocculent precipitate. Our earlier analyses of this substance gave varying results, due, it may be, partly to impurities, but doubtless largely attributable to its avidity for moisture and the difficulty of drying it completely or of holding it at a constant moisture content.

We could obtain no accordant analyses except by weighing off in quick succession several portions of the air-dry substance that had been fully exposed to air and was neither gaining nor losing moisture, determining carbon and hydrogen in some of these portions and moisture in others, with such precautions as to preclude change of water content.

Hygroscopic water we determined most satisfactorily by drying *in vacuo* at  $110^{\circ}$ – $112^{\circ}$  C. For this purpose the substance was contained in a stout glass tube about three cm. wide and ten cm. long, sealed off round at the base and narrowed above to a neck two cm. wide. This was connected by a perforated cork with a water pump, giving a vacuum equal to twenty-eight to twenty-nine and one-half cm. of mercury column, and was heated by placing within a close fitting vertical well, whose sides and bottom were surrounded by boiling aqueous solution of sodium nitrate contained in a closed copper box, the vapor from which was constantly returned by means of an efficient condenser. The glass drying tube, well corked, was counterpoised on the balance by a similar corked tube, and suitable precautions were used to avoid or compensate any changes of moisture of glass or corks.

Recurring to the already published statements, we note that the chemists whose analyses gave results mostly agreeing fairly with the formula  $C_6H_{10}O_6$ , are silent (in the accounts I have been able to refer to) as to their mode of drying, so Thomsen and Koch, or as in case of Wheeler and Tollens, analyzed "substance that had been dried over sulphuric acid and warmed for some hours at  $97^{\circ}$  in a water oven."

Mr. Winton, in this laboratory, found that two samples of finely subdivided air-dry wood gum from maize cobs required six days exposure to concentrated and recently boiled oil of vitriol to come to constant weight, with loss of 8.10 per cent. and

8.11 per cent., and thus dried further lost in three and one-half hours at 100° in a current of dried hydrogen in one case 0.67 per cent., and in another 1.83 per cent., and on further heating in hydrogen for two hours at 120°, lost 0.07 and 0.25 per cent. respectively.

But while it may not be difficult to bring wood gum nearly to complete dryness in the water oven, it is not easy to weigh off, transfer to a combustion tube and burn this dried substance without its taking up sufficient moisture to vitiate an analysis, especially when the atmosphere is humid.

In 1880, Dr. Jenkins, following the methods then in use in this laboratory, made his first analyses of air-dry xylan, determining water by prolonged drying in a water oven. In three combustions he obtained, reckoned on dry matter, 45.25, 45.48 and 45.72 per cent. of carbon respectively. His hydrogen determinations, however, were more irregular, *viz.*: 6.37, 7.35 and 5.90 per cent.

Dr. Jenkins next imperfectly dried his stock of xylan at 100° and weighed off the portions for analysis as required. In four combustions, reckoned ash free, carbon ranged from 44.34 to 45.20 per cent., and hydrogen from 5.92 to 6.01. His averages were: Carbon, 44.81; hydrogen, 5.96. These results are quite like those from which Thomsen, Koch, and Wheeler and Tollens, deduced the formula  $C_6H_{10}O_4$ .

Subsequently in 1883, Mr. (now Professor) Milton Whitney, devoted considerable time to analyses of various preparations of wood gum, sometimes using air-dry material, at others substance dried at 100°, but without reaching altogether satisfactory results.

Finally, after I, with Mr. Winton's aid, had accurately ascertained the conditions for completely desiccating this substance and the precautions needful in handling it, it became easy to fix its composition.

In 1885 Dr. Osborne made analyses of a sample of wood gum prepared by Mr. Whitney from corn cobs, being a first fraction thrown down by adding about one-half the amount of alcohol needful for complete precipitation of the soda-lye extract, and otherwise treated as before described. About two grams of this xylan required in one case near six hours heating at 112° in a

vacuum maintained at 29.0 to 29.5 inches mercury, and in another case when the vacuum ranged from 28.5 to 28.0 inches, needed nine hours heating at 112° for reaching constant weights. In either case the loss was 13.51 per cent., and further heating for three hours occasioned no change either in the weight or color of the substance.

Dr. Osborne's combustions of air-dry substance furnished results as follows :

	I.	II.	III.	Average.
Carbon.....	39.12	39.10	39.06	39.09
Hydrogen.....	6.81	6.65	6.73	6.73
Ash.....	0.59	0.66	0.59	0.61
Moisture .....	....	....	....	13.51

The above average reckoned on dry and ash-free substance is :

		Calculated for $C_5H_8O_4$ .
Carbon .....	45.51	45.45
Hydrogen .....	6.09	6.16
Oxygen .....	48.40	48.49
	100.00	100.00

In another similar preparation Dr. Jenkins demonstrated the absence of nitrogen by soda lime combustion.

In two other preparations the ash contents were found to be respectively 0.23 and 1.73 per cent.

At my request Mr. E. B. Hurlburt has lately hydrolyzed corn cob xylan prepared in 1880 and obtained a syrup which, after seeding with a little pure xylose,<sup>1</sup> in a few days, nearly solidified to a mass of crystals that when washed with alcohol and dried, melted at 153° C.

It thus appears that the cobs of Indian corn yield very pure xylan,  $C_5H_8O_4$ .

It is also probable that many of the analyses of wood gum hitherto published, those of Schuppe possibly excepted were made on imperfectly dried material, and for that reason mainly, gave results leading to the incorrect formula  $C_6H_{10}O_5$ .

*Birch Wood Gum.*—Preparations obtained from the wood of the American white, or gray birch, *Betula alba*, differ in compo-

<sup>1</sup> Kindly supplied for this purpose by Prof. W. E. Stone, who was the first to announce the preparation of xylan and xylose from maize cobs.

sition from the xylan of maize cob. Dr. Osborne found in the air-dry substance of one sample :

	I.	II.	Average.
Carbon.....	42.69	42.49	42.59
Hydrogen.....	6.65	6.59	6.62
Ash.....	0.65	0.64	0.65
Moisture.....	....	....	9.84

Moisture was determined by drying *in vacuo* at  $112^{\circ}$  C. Constant weight was obtained in one determination in six hours with 29.5 inches of mercury in manometer, the loss being 10.26 per cent., and in another in twelve hours with twenty-eight inches of mercury, the loss being 9.42 per cent.

The average results reckoned on substance free from moisture and ash are :

		Calculated for $C_4H_4O_3$ .
Carbon .....	47.58	47.06
Hydrogen .....	6.17	5.88
Oxygen .....	46.25	47.06

These figures for carbon are two per cent. higher than those belonging to the pentosans, and come nearer the composition of a tetrosan.

The birch wood gum, when hydrolyzed, yields a syrup from which, on long standing, or by fractioning with alcohol, a very small proportion of crystals may be separated, which do not appear to be increased in quantity by "seeding" with crystallized xylose.

The further study of birch wood gum and the products of its hydrolysis is reserved.

**Mannan.**—When the sugar obtained by Reiss' from vegetable ivory, the fruit of *Phytelephas*, as the result of hydrolysis, was shown by E. Fischer to be mannose, it became evident that the substance yielding this sugar is a carbohydrate of composition corresponding to the formula  $C_4H_{10}O_5$ .

According to Reiss,<sup>1</sup> vegetable ivory yields near seven and five-tenths per cent. of a water-soluble carbohydrate, which in the dry state is a yellowish brown gummy mass, having left-handed polarization, readily hydrolyzed and then yielding the

<sup>1</sup> *Ber. d. chem. Ges.*, 22, 609.

<sup>2</sup> *Landwirtschaftliche Jahrbücher*, 18, 745, 1889.

sugar mannose. The vegetable ivory also contains or yields, according to Reiss, a carbohydrate in large proportion, which he prepared as a white amorphous powder by digesting vegetable ivory shavings with an equal weight of seventy per cent. sulphuric acid for twenty-four hours, then adding to the mixture its weight of water, filtering, adding a little alcohol to throw down impurities, and lastly precipitating with mixed alcohol and ether, washing and drying the product. This substance, which Reiss found to swell and partially dissolve in water, and to be laevorotatory and to reduce Fehling's solution, was termed by him seminin and by Tollens' paramannan. It yielded mannose on hydrolysis, but its composition, so far as I am aware, has not been determined.

Several investigators have inferred the existence of mannan in seeds of coffee, date, nux vomica, *Diospyros*, cocoanut, and pine wood, etc., from the formation of an insoluble hydrazone in the products of the hydrolysis of these materials, but only Reiss, I believe, has attempted to separate the carbohydrate from the associated substances.

In the year 1880 a quantity of refuse vegetable ivory was sent to this station for examination, with the statement that "it had been used as feed for cattle, which ate it with great relish and fattened upon it."<sup>2</sup>

A "fodder analysis" was accordingly made, the results of which were as follows :

Water (at 100° C.).....	18.78
Ash .....	1.08
Crude fat (ether extract) .....	0.70
Albuminoids (N × 6.25) .....	3.37
Crude fiber.....	7.50
Nitrogen-free extract (by difference) .....	68.57

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100.00

It was at the same time found that vegetable ivory yields to

<sup>1</sup> Ladenburg's Handwörterbuch, 13, 755.

<sup>2</sup> Loew and Ishii have recently stated that the root of *Conophallus konnyaku*, which is used as human food in Japan, contains mannan, *i. e.*, yields mannosehydrazone in considerable quantity. (Versuchsstationen, 45, 435.) Salep mucilage, formerly used as food for invalids, also very probably contains mannan or a mannocellulose. (Gans and Tollens : *Ann. Chem.* (Liebig), 249, 256.)



soda lye a large proportion of substance resembling "wood gum," and a number of preparations were made in 1880 by Dr. Armsby, and in 1883 by Mr. (now Professor) Milton Whitney.

Mr. Whitney also analyzed six of these preparations. His mode of drying was long exposure to concentrated sulphuric acid and subsequent heating for one hour in the water oven.

The results of these analyses were not altogether uniform, but either by excluding extremes or taking the average they fairly agreed with the formula  $4(C_6H_{10}O_5)H_2O$ , which requires two and seven-tenths per cent. of hydrate water. This water, however, was doubtless merely hygroscopic.

After having ascertained the precise conditions for determining moisture in various specimens of wood gum, I requested Dr. Osborne in 1885 to analyze two of Dr. Armsby's vegetable ivory preparations then remaining. To determine moisture the air-dry material was heated *in vacuo* (28.0 to 29.5 inches of mercury) at  $112^\circ$  C. for eight to nine hours to constant weight. In one case the substance was further heated for three hours without change in weight or appearance.

The combustions were made on portions of the same air-dry substance as served for estimating moisture.

The following are Dr. Osborne's results:

SAMPLE B. I 2, AIR-DRY.

	I.	II.	III.	IV.	Average.
Carbon.....	....	....	40.08	40.17	40.13
Hydrogen.....	....	....	6.82	6.82	6.82
Ash.....	....	....	0.10	0.16	0.13
Moisture .....	9.59	9.65	....	....	9.62

SAMPLE B. II. 1, AIR-DRY.

	I.	II.	III.	IV.	Average.
Carbon.....	....	....	39.14	39.19	39.17
Hydrogen .....	....	....	6.92	6.90	6.91
Ash .....	....	....	trace	trace	trace
Moisture .....	10.88	10.88	....	....	10.88

The dry ash-free mannan has accordingly the subjoined composition:

	B. I. 2.	B. II. 1.	Calculated for $C_6H_{10}O_5$ .
Carbon .....	44.46	43.95	44.44
Hydrogen.....	6.37	6.39	6.17
Oxygen.....	49.17	49.66	49.38
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The mannan of vegetable ivory may be separated in fractions by adding alcohol to its solution in sodium hydroxide.

Armsby's preparation B. I. 2 and B. II. 1 were obtained as follows: One kilo of vegetable ivory turnings was digested for twenty-four hours in a mixture of 800 cc. concentrated ammonia and five and a half liters of water and washed with water until ammonia was removed. The residue was digested twenty-four hours in a solution of 800 grams potassium hydroxide in eight liters of water and filtered, giving a first extract B. I. The undissolved substance was then treated for twenty-four hours with a solution of 480 grams potassium hydroxide in six liters of water and filtered. The second extract was marked B. II.

The potash extract B. I. was mixed with about three-sixteenths of its bulk of ninety-three per cent. alcohol, and allowed to stand an hour; the turbid liquid was separated from the precipitate by decantation and filtration. This first precipitate was B. I. 1. The filtrate therefrom was completely precipitated by its own volume of alcohol, and the second precipitate was B. I. 2, whose analyses correspond so closely to  $C_6H_{10}O_5$ .

The soda extract B. II. with rather more than one-fourth its bulk of alcohol gave B. II. 1, (containing five-tenths per cent. less carbon than B. I. 2), and the filtrate therefrom with excess of alcohol yielded a second small precipitate B. II. 2.

These precipitations, after removing mother liquors, were washed with sixty-six per cent. alcohol until nearly neutral, then digested with excess of dilute hydrochloric acid for a day and finally washed out completely with sixty-six per cent., eighty per cent. and absolute alcohol and with ether in succession.

It thus appears that vegetable ivory may yield to dilute caustic alkali solutions a nearly or entirely pure mannan, and that this body is probably accompanied with an alkali-soluble substance of lower carbon content.

## METHOD FOR THE DETERMINATION OF CARBON IN STEEL.

BY ANDREW A. BLAIR

Received January 14, 1896.

THE method given below for the determination of carbon in steel is generally used in the steel works laboratories in the Eastern part of France, and I am indebted for the details to Monsieur H. A. Brustlein of the Aciéries d'Unieux at whose words and at those of the Aciéries de la Marine at Saint Chamond the various improvements in the method have been worked out.

The method was first suggested by Wiborg<sup>1</sup>, but was very imperfect in its original form. The greatest improvement was suggested by Monsieur de Nolly of the Laboratory of the Aciéries de la Marine at Saint Chamond and consists in the addition of phosphoric acid to the oxidizing mixture by which the iron is much more rapidly dissolved and the use of a considerable amount of chromic acid is rendered possible without the evolution of a large volume of oxygen gas.

The solutions employed are :

1. A saturated solution of chemically pure cupric sulphate.
2. An aqueous solution of chromic acid (one gram chromic acid to one cc. water).
3. A mixture of sulphuric, phosphoric and chromic acid made up as follows.

Solution of chromic acid (Sol. No. 2).....	35 cc.
Water .....	115 "
Concentrated sulphuric acid .....	750 "
Phosphoric acid 1.4 sp. gr. ....	315 "

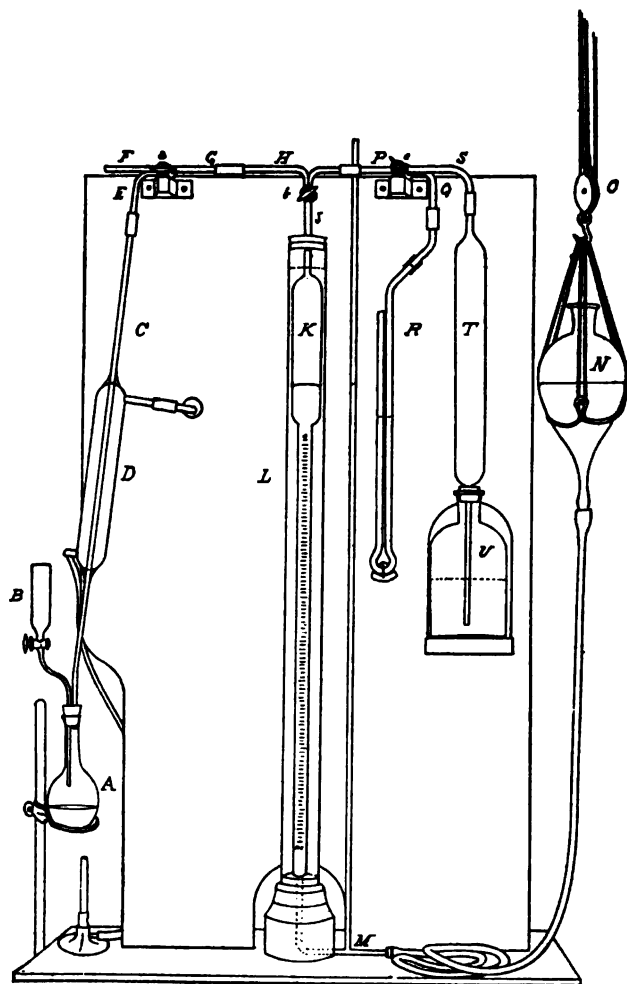
In preparing solution No. 2, add a few cc. of sulphuric acid and heat to boiling to destroy any organic matter that may be present.

In preparing solution No. 3, heat it to boiling also for the same purpose.

The apparatus as shown in the sketch consists of a round bottom Flask *A* of 200 cc. capacity with a long neck. The flask is closed with a rubber stopper with two holes, in one of

<sup>1</sup>Stahl und Eisen, 1882.

which is fitted the glass stopper funnel *B* and in the other the tube *C* enclosed in the condenser *D* through which a stream of water runs during the operation. The tube *C* is connected with



one tube *E* of a three way stopcock *a*, from which the second tube *F* opens into the air and the third *G* connects with the tube *H* of the three way stopcock *b*. The second tube *J* from

this stopcock is fused to the burette *K* which is enclosed in the tube *L* containing water. The lower end of the burette connects with a capillary tube *M* which serves as a level tube and is in the form of a J; it is connected with the mercury reservoir *N* which is raised and lowered by the arrangement *O*. The third tube of the stopcock *b* connects with the tube *P* of the stopcock *c*, the second tube *Q* of the stopcock *c* connects with the manometer *R* and the third tube *S* with the pipette *T* which runs into the bottle *U*. The tubes of the stopcocks *b* and *c*, the manometer tube *R*, the level tube *M* and the tubes of the pipette *T* are capillaries. The manometer tube *R* contains water and serves to accurately adjust the levels when taking the reading of the burette *K*. When the manometer is shut off from the burette the approximate level is ascertained by means of the level tube *M*. The tube *F* of the stopcock *a* is used only in exceptional cases: First, when the evolution of gas is insufficient to carry the mercury far enough down the burette *K*, in which case air is drawn through it into the burette; and secondly, when the evolution of gas is so great that it is necessary to make two absorptions in the pipette *T*, in which case the residue from the first absorption is discharged through the tube *F*. The pipette *T* contains a solution of potassium hydroxide of 1.27 sp. gr., it is of about 400 cc. capacity. The bottle *U* is of about one liter capacity. The water in the containing tube *L* serves to keep the gas in the burette at the ordinary temperature of the laboratory. It should be protected from the heat of the burner and flask by a screen.

The operation is conducted as follows:

Connect the pipette *T* by means of the stopcocks *b* and *c* with the burette *K* and, by lowering the mercury reservoir, fill the pipette with the potassium hydroxide solution, close the stopcock *c*, fill the burette *K* with mercury and close the stopcock *b*. Weigh one gram of drillings into the flask *A*, attach it to the apparatus, start the water through the condenser *D*, and connect the flask with the burette *K* by means of the stopcock *a*. Pour fifteen cc. of the cupric sulphate solution No. 1 into the funnel tube *B*, and let it flow into the flask. Allow it to act long enough to form a superficial deposit of copper on the

drillings (one or two minutes is sufficient) then add, through the funnel tube, fifteen cc. of solution No. 2 and 135 cc. of solution No. 3. Heat the solution in the flask and raise it slowly to the boiling point. By means of the reservoir, keep the mercury in the burette and in the tube *M* nearly level. The water condensed in the tube *C* drops back into the flask and keeps the liquid of the same density, while the properly cooled gases pass into the burette.

Allow the flask *A* to cool for about five minutes and then run into it, through the funnel tube *B*, enough water to fill the flask and the tube to the stopcock *a*, thus forcing all the gas into the burette. Close the stopcock *a* and connect the burette by means of the stopcocks *b* and *c* with the manometer *R*, adjust the levels accurately and take the reading of the burette. Then by means of the stopcock *c* connect the burette with the pipette *T* and by raising and lowering the reservoir *N*, pass the gas several times back and forth to cause the potassium hydroxide to absorb all the carbon dioxide. Finally connect the burette with the manometer tube *R*, adjust the levels and take the reading of the burette.

The burette *K* should contain a few drops of water to insure the saturation of the gases with aqueous vapor. The difference between the two readings is the volume of the carbon dioxide. Observe the readings of the thermometer and barometer and reduce the volume of the carbon dioxide to that which it would occupy in the dry state at 0°C. and 760 mm. pressure.

Multiply the volume of the gas so obtained by 0.0019663 and the result is the weight of the carbon dioxide in grams.

I have constructed the apparatus as here described, and am satisfied that the results obtained by its use when the details of the method are carefully carried out are much more accurate than those arrived at by any other than the combustion method. Blank determinations at Unieux rarely give more than one-tenth cc. or two-tenths cc., when the solutions are properly purified. As results may be obtained in an hour and a half, the method should recommend itself to the chemists of steel works where determinations of carbon are called for in treated and special steels where the color method is inadmissible.

It may be noted here that the use of a condenser and the solutions given above will add to the accuracy of the method in which the carbon dioxide is weighed instead of measured.

LABORATORY OF BOOTH, GARRETT & BLAIR,  
PHILADELPHIA.

## A NEW SAFETY DISTILLATION TUBE FOR RAPID WORK IN NITROGEN DETERMINATIONS.

BY CYRIL G. HOPKINS.

Received December 12, 1895.

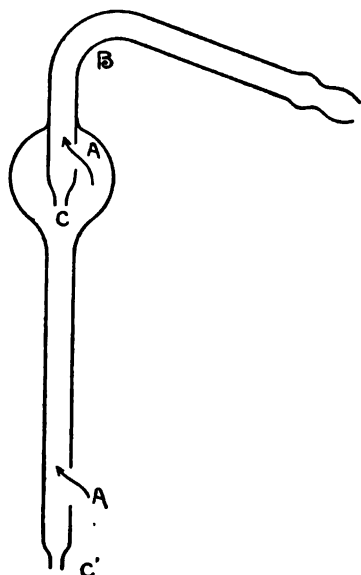
IN doing a large amount of work with fodders and fertilizers, involving several hundred determinations of nitrogen (by the Kjeldahl method), I have observed that the distillation tube (generally known as "Kjeldahl's connecting bulb tube," but doubtless more properly as Reitmeir's distillation tube) is frequently a source of error, due to the fact that it allows fixed alkali to be carried over mechanically. Especially is this the case when the distillation is carried on rapidly, and also when the contents of the distillation flask has a tendency to "bump."

In doing rapid work I have always found it necessary to have the lower end of these tubes reground before they would allow the liquid condensed in the bulb to run back into the distillation flask. Even after this is properly done the lower end of the tube is still open, and when the liquid boils violently or "bumps," small particles of it are often thrown up through the tube into the bulb. Sometimes these particles of strongly alkaline liquid strike the curved tube within the bulb, flow out to the end, and are forced into the tube and over into the condenser by the rapid current of vapor. This action is easily observed when the contents of the distillation flask is highly colored; and I find that the occurrence is familiar to chemists who have had much to do with nitrogen determinations.

I have obtained good results, however, by having the end of the tube within the distillation flask properly ground, and then protected by a larger glass tube, fastened to the distillation tube just below the rubber stopper, by means of a short piece of rubber tubing, and having an opening on the side and a jet at the lower end. This modification gave such good satisfaction that it finally led me to make a new distillation tube in which

not only the tube which passes into the distillation flask, but also the tube within the bulb has an opening on the side and a jet at the end.

The form of this distillation tube and its advantage



tube in ordinary use will be plainly seen in the accompanying illustration.

The vapor passes in through the side openings *A* and *A'*, and whatever condenses in the tube below the point *B* passes back into the distillation flask through the jets *C* and *C'*.

The possibility of liquid from the distillation flask being thrown into the tube is avoided, and the current of vapor does not interfere with the return of condensed liquid. The jets *C* and *C'* are two mm. inside diameter and they always remain filled with returning liquid when in

use. The tubing used in making these distillation tubes is from seven mm. to eight mm. inside diameter. The side openings *A* and *A'* should be nearly as large, and the bulb about five cm. in diameter. The length of the tube below the bulb is twelve cm. and that above the bulb about the same.

UNIVERSITY OF ILLINOIS, EXPERIMENT STATION.

## REMARKS ON MR. AUCHY'S PAPER ON THE VOLUMETRIC DETERMINATION OF MANGANESE.<sup>1</sup>

BY GEORGE C. STONE.

Received January 11, 1896.

IN the December number of the Journal of the American Chemical Society there is a paper by Mr. George Auchy on the "Volumetric Determination of Manganese," in which he advocates the use of Volhard's method, in which I heartily agree

<sup>1</sup> Read before the New York Section.



with him, but the method as he describes it, seems to me unnecessarily complicated.

Mr. Auchy criticises Williams' method and refers to the discussion of it which occurred some years since.<sup>1</sup> At that time I satisfied myself that the method as originally described by Williams was not accurate, but in a modified form I used it for several years with good results until I, too, was treated to the same disagreeable surprise as Mr. Auchy, a number of manganese determinations came very low. On examination I found that this was due to the decomposition of the oxalic acid solution. I then gave up the method and have since used Volhard's with uniformly satisfactory results, except where there are only a few hundredths of a per cent. of manganese present, in which case I found the method of oxidizing by peroxide of lead, reducing by standard arsenious acid and titrating back by permanganate to work well.

Volhard's method, as I have used it, is as follows: The quantity of material taken for analysis should contain between 0.05 and 0.15 grams of manganese. If it is an alloy, dissolve in nitric acid of about 1.10 sp. gr.; if an ore or cinder, dissolve in hydrochloric acid and boil with a little potassium chlorate. In either case use but a small excess of acid. Cool, wash into a half liter flask with cold water and add an emulsion of zinc oxide until the precipitate curdles; the change in the appearance of the precipitate is sharp and distinct. Dilute to the mark, mix thoroughly, pour into a beaker and allow the precipitate to settle. Decant off exactly 100 cc. into a four inch casserole, dilute to about 200 cc., heat nearly to boiling and titrate rapidly with permanganate, one cc. of which should equal 0.001 gram of manganese (about 1.99 grams potassium permanganate in one liter). The greater part of the permanganate should be added at once and the solution very vigorously stirred. For this purpose a glass rod bent to a hook is very convenient, the hook, of course, being in the solution.

I have made a number of experiments to see if it makes any difference whether nitric, hydrochloric or sulphuric acid is used, and have not found that it does, provided the iron is oxidized. For

<sup>1</sup> Trans. Am. Inst. Min. Eng., 11, 514; 12, 295-449; *Chem. News*, 1883, 176-273.

neutralizing I use commercial zinc oxide, which contains a trifling amount of manganese, but under the conditions in which it is used this apparently does not go into solution. To test this point, I made a number of duplicate analyses, neutralizing one of each pair with zinc oxide and the other with barium carbonate; in all cases the results agreed well. It is not necessary to filter the solution, the iron precipitate settles very rapidly and completely, and if a little of the precipitate goes with the solution, it makes no difference. I think the trouble Mr. Auchy mentions in getting good results with steels low in manganese when a large excess of zinc oxide is used, is due to not having sufficient manganese present, as it is difficult to make a very small precipitate clot together so as to give a clear solution in which the color of the end reaction shows distinctly. I have often tried adding a very large excess of zinc oxide, but have never found it to interfere, provided the manganese was within the limits given above.

The method is very rapid, a determination of manganese in spiegel can easily be made in half an hour; ores usually take a little longer, as they are more difficult to dissolve.

#### PROBABLE PRODUCTION OF PERMANGANATE BY DIRECT COMBUSTION OF METALLIC MANGANESE.<sup>1</sup>

BY GEORGE C. STONE.

Received January 11, 1896.

WHEN casting at a Spiegel furnace, a good deal of iron and manganese is always burned at the tap hole, giving a very hot flame and clouds of reddish fume, the hotter the furnace and the higher the percentage of manganese in the iron, the more sparks and fume. To protect themselves from these sparks the men often put a sheet iron screen over the run and tap holes. One day some water was accidentally spilled on this screen immediately after casting. It at once took the deep purple color of a permanganate solution; unfortunately the screen was upset and the solution spilled before I could secure any of it for further examination. At the time the furnace was working very hot, making a high grade spiegel and a basic cinder.

#### DISCUSSION.

Dr. Rosell called attention to the fact that potassium permanganate when heated to a red heat would decompose, and that the

<sup>1</sup>Read before the New York Section.

other permanganates behave in the same way. In fact the permanganates can only be made in the wet way. On the other hand, manganates are generally produced in the dry way, and they will stand a very high temperature.

If, therefore, a substance, after having been heated to the temperature of the blast furnace, would dissolve in pure water with the well known rich purple color of a permanganate solution, it seems almost certain that such a substance could not be a permanganate, but it could be a solution of a ferrate. It is, of course, also possible that the water used to dissolve the substance in question was not pure, but accidentally contained some acid, whereby, on dissolving, the manganate was converted into permanganate.

### THE MANUFACTURE OF ACETONE AND OF ACETONE-CHLOROFORM FROM ACETIC ACID.<sup>1</sup>

BY EDWARD R. SQUIBB.

Received January 25, 1896.

JUST one year ago, January 11th, 1895, the writer read a paper before this Society upon "Improvement in the Manufacture of Acetone," and this paper was published in the Journal for March, 1895, page 187. The improvement claimed consisted in the use of acetic acid, instead of acetates, and in the use of a rotary still for the decomposition. The results given were obtained from a model apparatus on a table.

During the year that has elapsed since that paper was read, a large rotary still, twelve feet in length by two feet in diameter, has been set up, and this has decomposed in 126 hours about 1,700 pounds of absolute acetic acid, giving about ninety per cent. of the theoretical yield of acetone against about eighty per cent. in the small apparatus.

But the patentees of the processes for making acetone from acetates object to the use of this process and apparatus as being in conflict with their patents.

The acetone produced was converted into chloroform by the Watts (Seimerling) proportions of material in an apparatus described by the writer in 1857,<sup>2</sup> and used for many years in making chloroform from alcohol, and this is also objected to.

<sup>1</sup> Read before the New York Section, January 10, 1896.

<sup>2</sup> *Ephemeris*, 4, [1], 71.

Under these circumstances it seems necessary to find out what has been done in the past upon this important subject, and what may be the relations of past work to the present conditions, and in this it is hoped the society may be interested.

#### ACETONE.

It is impossible to determine when or where acetone was first made and used.<sup>1</sup> According to the authority last given, after the time of Boerhaave in 1732, "the body was but little investigated until 1805, when Trommsdorff stated that on distilling acetate of potash or soda, a liquid was obtained which stands between alcohol and ether." In 1807 the Brothers Derosne in Paris<sup>2</sup> studied its properties; and in 1809 Chenevix<sup>3</sup> demonstrated that this substance was obtained by the dry distillation of any one of the acetates.

The correct composition of acetone was first given by Liebig<sup>4</sup> and Dumas.<sup>5</sup>

Further investigations by Kaue, 1838, and by Chancel, Williamson, Chiozza, Freund, Wanklyn, and others, still more definitely established the sources, character and properties of acetone, and gave it a definite chemical and economic position so that its production or manufacture by the dry distillation of acetates was as well known as the production of alcohol by distillation from fermented sugars, as early as 1848, when Böttger refers to it as a market article in common use. Wackenroder,<sup>6</sup> in 1848, states that since acetone is quoted on the price lists at ten sgr. (Silbergroschen) per ounce, the preparation of chloroform from it is well worth recommending.

In "Handwörterbuch der reinen und angewandten Chemie herausgegeben von Dr. J. Liebig, Dr. J. C. Poggendorff und Dr. Fr. Wöhler—Redigirt von Dr. Hermann Kolbe, Braunschweig," 1842, Vol. II, p. 1018, is the following (translated) statement:

According to Justus Liebig and Pelouze, the best thing to use

<sup>1</sup> See Wurtz' *Dictionnaire de Chimie*, 1873, 1, 31; Gmelin: *Handbook of Chemistry*, 1855, 9, 1; Roscoe and Schorlemmer: *A Treatise on Chemistry*, 1882, 3, [1], 568.

<sup>2</sup> *Ann. de Chim.*, 63, 267.

<sup>3</sup> *Ann. der Phys.*, 32, 191.

<sup>4</sup> *Ann. Pharm.*, 1, 223.

<sup>5</sup> *Ann. Chim. Phys.*, 49, 208.

<sup>6</sup> *Archiv. der Pharm.*, 53, 273.

for the preparation of acetone is concentrated acetic acid, which in the state of vapor is conducted through a heated tube of glass, porcelain or iron, which for the sake of increasing surface, is filled with pieces of charcoal, and the products of decomposition are condensed in the usual way. The tube should be heated only to incipient redness; at a higher temperature only empyreumatic oils, combustible gases and charcoal are obtained as the products of the decomposition.

Beside the citations given, the literature on the preparation, properties and reactions of acetone is very copious and definite up to about 1853. After this date the papers published are comparatively few, leading to the inference that the substance had reached a definite position and gone into general use.

In a paper by Prof. Samuel P. Sadtler, Ph.D., "On Recent Improvements in the Methods for the Manufacture of Chloroform," published in *The American Journal of Pharmacy* for July, 1889, p. 321, the following statements are made:

"The old process of manufacture by the action of bleaching powder upon alcohol has given way to what is now termed the 'acetone' process. This is not, however, a new discovery. Liebig, in 1832, in following up his first account of the properties of the newly discovered "chloride of carbon" (chloroform) mentions that it can be gotten in very large quantities by the action of bleaching powder upon 'pyroacetic spirit' (acetone) as well as from alcohol. That alcohol has all this time been preferred to acetone as a material from which to prepare chloroform is due mainly to the fact that only in recent years has acetone been prepared pure in quantity, but also to the erroneous statement of Siemerling, quoted in the works of reference like Watts' Dictionary of Chemistry, that only thirty-three per cent. of chloroform could be gotten from acetone by the action of bleaching powder." . . . "The manufacture of a purer grade of acetone than that then in use for solvent purposes, having been begun in Germany in 1881, on the part of the 'Verein für Chemische Industrie.' Liebig's old suggestion for the manufacture of chloroform from acetone was taken up by the 'Verein Chemischer Fabriken,' Mannheim, Germany, in the beginning of 1882, and a year later by the first mentioned company which made the acetone for both."

From these references it will be seen that the reactions involved in the production of acetone, and the constitution, character, properties and reactions of acetone had been long and well known prior to 1848, and that it had been made and utilized on a large scale prior to 1882; and further, that it had been produced both by the dry distillation of acetates, and by the wet distillation of acetic acid, as a matter of open knowledge and practice.

This condition of the scientific knowledge of an important chemical substance throughout France and Germany—and throughout the scientific world—makes it very certain that the chemical industries, which depend upon such knowledge for their origin and progress in general, but do not publish their processes—availed themselves of this knowledge and of this chemical agent.

In June, 1886, application was filed in the U. S. Patent Office, and two years later, in July, 1888, Letters Patent No. 385,777 were issued to Gustav Rumpf for the invention of a "new and useful Improvement in the Manufacture of Acetone," and from the specifications and claims of this patent the following extracts are made:

"In making acetone by dry distillation of acetates, as acetate of lime, it has, before my invention, been thought possible to obtain only less than half the acetone."

"Dr. Herman Hager, in his *Handbuch der Pharmaceutischen Praxis*, published in Berlin in 1882, states under the head of 'Acetone,' 'that it is possible to obtain an average yield from chemically pure acetate of lime of only fifteen per cent. of acetone, while the theoretical yield from chemically pure acetate of lime is thirty-four per cent.'"

"I have discovered that if the acetates are subjected for distillation to a low heat and approximately uniform temperature and the process extended over several hours, the yield of acetone will be greatly increased, and will approach very nearly the theoretical yield of any particular acetate, which in the case of good gray or commercial acetate of lime is about twenty-seven per cent. I have also discovered that in the process of subjecting acetates in a closed vessel to heat applied externally to the vessel

for distilling acetone from the acetates the desired slowness of distillation and uniformity of temperature may be secured by stirring the acetates so that all portions of the mass will be subjected to the heat resulting from direct contact with the bottom of the vessel, and by admitting free steam from time to time into direct contact with the acetates in case of any undesirable rise in temperature within the vessel."

"My invention consists in an improvement in the method of obtaining acetone from acetates by destructive distillation, consisting in subjecting the acetates in a closed vessels to slow destructive distillation at a low and approximately uniform temperature, and it is also well to stir the acetates during such distillation."

The claims are to—

"The improvement in the method of obtaining acetone from an acetate consisting in subjecting the acetate in a closed vessel to slow destructive distillation at a low and approximately uniform temperature."

This first broad claim is based, not upon the chemical reaction which was well known, nor upon the destructive distillation by heat, which was a well known process, but upon an improvement in the apparatus and management by which the yield of acetone was alleged to have been increased. But the evidence upon which the increase is claimed is an erroneous statement quoted from Hager—erroneous because it is hardly practicable through any ordinary degree of want of knowledge and skill to obtain so little as fifteen per cent. of acetone from acetate of lime.

The second claim is to a stirrer in its effects on the process. But a stirrer is a device so common in chemical processes that no such application of it can be considered original or new.

The third claim to the effect of the introduction of steam during the distillation is much better.

The fifth, sixth, seventh and eighth claims are to improvement in the process of purifying the crude acetone by means of lime, dilution and rectification, and these are but the steps common to all such operations.

It is upon this patent that infringement is charged, when it is

simply putting into use the very old process of making acetone by the destructive distillation of acetic acid in a rotary still as described in a paper on "Improvement in the Manufacture of Acetone," read before this New York Section of the American Chemical Society on January 11, 1895, and published in the *Journal* for March, 1895, p. 187, and in *An Ephemeris of Materia Medica, Pharmacy, Therapeutics and Collateral Information*, Vol. IV, No. 3, p. 1653.

The writer makes acetone by the destructive distillation of the watery vapor of acetic acid in a rotary still, in the presence of barium carbonate or pumice-stone or bone-charcoal, barium carbonate being preferred, because being a very heavy powder, a larger charge of smaller volume can be used.

The patentees claim only acetates as their material, but claim infringement by the use of acetic acid, because acetic acid is made from acetates, and acetates are made from acetic acid; and secondly, claim infringement on the ground that acetate of barium is first formed, and then decomposed in the rotary still, and therefore the process is really not a destructive distillation of acetic acid, but of barium acetate—one of the class of acetates claimed as secured to them by their patent, although in use for this purpose for so many years. That is, it is claimed that an acetate of barium is formed under conditions of temperature in which an acetate of barium cannot exist. Barium acetate decomposes at about  $400^{\circ}$  to  $405^{\circ}$  C. by an ordinary pyrometer. Acetic acid is best decomposed at about  $500^{\circ}$  to  $525^{\circ}$  C. by the same pyrometer, and yet it is claimed that at  $500^{\circ}$  C. barium acetate forms momentarily and then is instantly decomposed. That is, it is formed in an atmosphere in which it cannot exist for an instant, and in which acetic acid cannot exist.<sup>1</sup>

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<sup>1</sup> Upon this point the patentees were very decided in the statement, based not only on their own experience, but also on the experience of their German correspondents, that if the barium carbonate was replaced by pumice-stone the amount of acetone obtained would be too small to have any commercial importance. This result had been confirmed to them by so many trials that at their suggestion, and in order to satisfy them that their results were not trustworthy, the following experiments were made after the above paper was written, but before it was published.

The large rotary still was emptied and cleaned out by sweeping, scrap-



But, quite apart from this, the chemical reaction by which acetone is produced, whether from acetates or from acetic acid, was well known for more than half a century before the date of this patent. What is really covered by the patent is certain specified and described apparatus and management whereby an improved yield is to be obtained from acetates, and from acetates only, for the apparatus and management are not at all applicable to the use of acetic acid, and are not used either in form or substance.

## ACETONE-CHLOROFORM.

The history of acetone-chloroform dates distinctly back to 1832. In the *Annalen der Pharmacie*, 1832, 21, 198, Liebig describes the preparation of chloroform in large quantity, from given proportions of hypochlorite of lime, water, and alcohol, and he says the yield will be equal in weight to the alcohol used. He then goes on to say that chloroform may also be obtained in large quantity by treating acetone with hypochlorite of lime under the same conditions.

ing, and finally by sponging with water until it was quite free from any appreciable quantity of barium salt. It was then closed and run empty with a continuous feed of acetic acid for periods of three hours each, at the following temperatures, the rate of feeding, and the assaying for acid and acetone being approximate only, and only trustworthy by averaging.

At 300° C.	22.3	pounds of absolute acid was run in and	
	19.5	" " " " " received without any acetone or any evidence of decomposition of the acid, the 2.8 pounds of acid not accounted for being the normal charge of the apparatus.	
At 350° C.	38.3	pounds of absolute acid was run in and	
	38.1	" " " " " came through with no signs of any decomposition,—no acetone.	
At 400° C.	36.1	pounds of absolute acid was run in and	
	29.9	" " " " " received undecomposed, leaving	
	6.2	" " " " " decomposed, and this decomposed acid gave	
		97 per cent. of the acetone required by theory.	
At 450° C.	35.1	pounds of absolute acid was run in and	
	18.5	" " " " " received undecomposed, leaving	
	16.6	" " " " " decomposed, which apparently gave 112 per	
		cent. of the acetone required by theory.	
At 500° C.	41.4	pounds of absolute acid was fed in and	
	10.8	" " " " " received undecomposed, leaving	
	30.6	" " " " " decomposed, which apparently gave 104 per	
		cent. of the acetone required by theory.	
At 550° C.	40.4	pounds of absolute acid was fed in and	
	5.1	" " " " " received undecomposed, leaving	
	35.3	" " " " " decomposed, which apparently gave 82 per	
		cent. of the acetone required by theory.	

Liebig does not give the yield from acetone, but after giving the yield from alcohol as being equal in weight to the alcohol used, he says it is obtained in large quantity from acetone.

In 1835 Dumas and Peligot<sup>1</sup> state that when a solution of hypochlorite of lime is distilled with wood spirit there is obtained, as a matter of fact, some ordinary chloroform. The experiment is as easy as with alcohol or acetone.

Then a run of twenty-four hours was made at the last temperature, 550° C. to give opportunity for closer determinations of results.

321	pounds of absolute acid was fed in and
57.3	" " " " " received undecomposed, leaving
263.7	" " " " " decomposed, which apparently
	gave 97 per cent. of the acetone required by theory.

The still was then opened, charged with 140 pounds of coarsely ground pumice-stone, and a parallel series of experiments made.

At 300° C.	41.8 pounds of absolute acid was fed in and
39.1	" " " " " received undecomposed, leaving
2.7	" " " " " decomposed, which apparently gave 33.5 per
	cent. of the acetone required by theory.

At 350° C.	39.6 pounds of absolute acid was fed in and
34.8	" " " " " received undecomposed, leaving
4.8	" " " " " decomposed, which apparently gave 87.5 per
	cent. of the acetone required by theory.

At 400° C.	41.8 pounds of absolute acid was fed in and
28.5	" " " " " received undecomposed, leaving
13.3	" " " " " decomposed, which apparently gave 97 per
	cent. of the acetone required by theory.

At 450° C.	41.8 pounds of absolute acid was fed in and
13.0	" " " " " received undecomposed, leaving
28.8	" " " " " decomposed, which apparently gave 95 per
	cent. of the acetone required by theory.

At 500° C.	43.4 pounds of absolute acid was fed in and
8.8	" " " " " received undecomposed, leaving
34.6	" " " " " decomposed, which apparently gave 96.4 per
	cent. of the acetone required by theory.

At 550° C.	43.4 pounds of absolute acid was fed in and
7.4	" " " " " received undecomposed, leaving
36.0	" " " " " decomposed, which apparently gave 100 per
	cent. of the acetone required by theory.

Then a run of twenty-four hours was made at the last temperature, 550° C., as a check upon the previous results.

345.5	pounds of absolute acid was fed in and
69.5	" " " " " received undecomposed, leaving
276.0	" " " " " decomposed, which apparently gave 104 per
	cent. of the acetone required by theory.

This last, and three other impossible results are as yet unexplainable, but they may be reasonably charged to the uncertainties in the use of an hydrometer and the iodoform process of assaying.

<sup>1</sup> *Ann. Chim. Phys.*, 58, 15.

Liebig in his text-book<sup>1</sup> gives a formula and directions for the manufacture of chloroform from either acetone, alcohol, or wood spirit, and gives to acetone the leading place.

M. Bonnet<sup>2</sup>, at a meeting of the Academy, says, "I have obtained in the distillation of equal parts of acetate of lime and hypochlorite of lime, in a stone retort, a very large quantity of chloroform, and far more easily than by the methods of preparation that are known.

Dr. Reich<sup>3</sup> proposed and used hypochlorite of sodium in place of hypochlorite of lime on account of the uneven amount of chlorine in the latter. He distilled together two pounds each of hypochlorite and acetate of sodium and received five to six drams of chloroform and twelve to fourteen ounces of acetone and water. This latter was again distilled with four to six ounces of hypochlorite, and again a considerable amount of chloroform and acetone was received. The last operation was repeated with a new portion of hypochlorite, and then the total amount of chloroform was eight to ten ounces, with still some excess of acetone for future operations.

Acetone when distilled with sodium hypochlorite yields chloroform in the proportion of four ounces of acetone to five to five and one-half ounces of chloroform.

Prof. Böttger<sup>4</sup> distilled together equal quantities of commercial bleaching powder and crystallized sodium acetate and obtained chloroform and acetone. Then he distilled the excess of acetone with a fresh portion of bleaching powder and had "great joy in seeing from this second operation a very considerable quantity of the purest chloroform distil over together with some acetone still undecomposed." The excess of acetone was again distilled with fresh bleaching powder and the process repeated until by three to four distillations all the acetone was used. The yield of chloroform being about four ounces to each pound of bleaching powder.

Chloroform made directly from acetone, which he says is at present, 1848, to be had in the market, is obtained in the propor-

<sup>1</sup> *Traité de Chimie Organiques*, 1, 576.

<sup>2</sup> *L'Institut*, No. 196 Februar, 1837.

<sup>3</sup> *Archiv. der. Pharmacie*, Zweite Reihe, 1848, 55, 65.

<sup>4</sup> *Polytechnisches Notizblatt*. 1848. 3, 1.

tion of one ounce and two drams of chloroform from one ounce of acetone.

Still in the year 1848 Prof. Heinrich Wackenroder,<sup>1</sup> one of the editors of the *Archiv*, says in substance: "The great practical interest in chloroform at the present time calls, first of all, for a closer examination of the methods for making it. Therefore I have induced Mr. Siemerling to undertake, in my laboratory, some experiments relating to the preparation of chloroform which are in the most recent publications on the subject. Although these experiments have in no respect given the results which were hoped for, it nevertheless seems to be worth while to call attention to them for the sake of the future continuation of the subject."

Then follows the paper of Mr. V. Siemerling, and at page 26: "II. Preparation of Chloroform from Acetone."

"According to the statement of Prof. Böttger, one ounce of acetone, which has been mixed with hypochlorite of lime to a pasty mass, should give one ounce and two drams of chloroform. As this seemed to be an easy and advantageous method of preparation, some experiments were made with acetone procured from the factory of Trommsdorff, in Erfurt, but they did not accord with the statement of Böttger."

"In the first experiment (*a*) thirty grams of acetone were mixed with fifty grams of hypochlorite of lime and fifty grams of water and distilled. The chloroform was separated and rectified with concentrated sulphuric acid. The yellow chloroform thus obtained was again rectified from burnt lime when it had an empyreumatic odor—quantity not given."

In experiment (*b*) thirty gram of acetone, 120 of hypochlorite and enough water to make a pasty mass, were mixed and distilled. It is true much chloroform came over, but there was also undecomposed acetone as well. It was repeatedly washed with water and rectified over calcium chloride, in which rectification there was a pretty large loss every time, but the number of times is not given. The yield was nine grams.

Experiment (*c*), since in both experiments undecomposed acetone distilled over the quantity (proportion) of hypochlorite was

<sup>1</sup> *Archiv. der Pharmacie*, 1848, 54, 23.

increased, and thirty grams of acetone to 150 grams of hypochlorite, with water, were mixed to a pasty mass, allowed to stand twenty-four hours, and were then distilled. The product contained much chloroform, but also undecomposed acetone; therefore it was put back into the retort with forty grams of fresh hypochlorite and again distilled. The chloroform thus obtained still contained acetone, from which it was purified by repeated washing with water, and then rectified over calcium chloride. The yield was ten grams of chloroform.

Another experiment (*d*) is given wherein twenty grams of acetone and sixty grams of hypochlorite were distilled together without water, but with unfavorable result, the yield being six grams of chloroform.

The specific gravity of the chloroform obtained from acetone, after repeated rectifications over calcium chloride was only 1.31, and it always contained some acetone; and the largest yield by Böttger's process was one-third of the acetone used. This differs considerably from his statement that one part of acetone yielded one and one-fourth parts of chloroform.

Siemerling then goes on to say, that if we assume with Liebig, that acetone is composed of one atom of acetyl oxide and one atom of methyl oxide, and explain in this way the formation of chloroform, from methyl oxide it naturally follows that we must get less chloroform than the acetone used.

The sum of the elements of one atom of acetyl oxide  $=C_2H_3O$  and one atom of methyl oxide  $=CH_3O$  is equivalent to two atoms of acetone  $=C_2H_4O$ . In thirty grams of acetone there are therefore 11.8 grams of methyl oxide, which, since four atoms of methyl oxide consist of the same elements as two atoms of alcohol, can form 15.1 grams of chloroform, assuming that complete decomposition takes place.

According to the theory, half of the acetone used must be recovered as chloroform; but since in the practical manufacture of chemical products the quantity prescribed by theory is never obtained, it should be considered a favorable result when one-third of the acetone used is obtained as chloroform, especially as the experiments were made only on the small scale.

From these experiments, it follows that the preparation of

chloroform from acetone is quite unfit for practical use. Were even the quantity of chloroform stated by Böttger as obtainable from acetone possible, it would have the disadvantage of being freed from acetone with very great difficulty.

The paper of Siemerling, from which the above abstract is made, seems to have received the endorsement of Wackenroder, although it controverts the statements of both Reich and Böttger, and it may be from his high authority as much as from the paper [itself] that the results seem to have been accepted and quoted by Gmelin,<sup>1</sup> Watts,<sup>2</sup> and other reference authorities, and the influence of the publication seems to have been, so far as the literature of the subject goes, to prevent or obstruct the acetone process for many years. As it was so long and so well-known, manufacturers may have been, and probably were using the process privately, but up to 1881-1883<sup>3</sup> very little information on the subject is found. Still the work and the conclusions of Siemerling must have been known to be grossly erroneous by every one whose interest it became to try them. Calculations would show to anyone that when ordinary acetone and bleaching powder were used the proportions required are about one to ten, or about double the largest proportion of hypochlorite used by Siemerling, and the resulting chloroform should be about double the weight of the acetone used; and many who preceded Siemerling knew better than he how to save and utilize the great excess of acetone, or deficiency of hypochlorite taken.

But the Siemerling results were very faulty and very misleading in other respects. The present writer having learned from all the work of the past on the subject, that any excess of acetone used could be easily recovered and used again, added to this knowledge from his own experience the fact, that, where an excess of acetone was taken, the hypochlorite was more economically and more promptly utilized, and the resulting chloroform was cleaner. Having gained from the Siemerling process this step the writer was prepared to try that proportion and process critically, and he found that, as a table experiment, it was

<sup>1</sup> Handbook of Chemistry, Vol. VII, 346.

<sup>2</sup> Dictionary of Chemistry, 1883, 1, 918.

<sup>3</sup> Sadtler, *Am. J. Pharm.*, July, 1889, 321.

quite impracticable by any reasonable degree of mismanagement to obtain so low a result. In two fairly careless trials from thirty grams of ninety-six per cent. acetone the yield of chloroform was twenty-three grams in one case and thirty-two grams in the other, instead of Siemerling's ten grams. In larger trials of his proportions up to 280 pounds of absolute acetone to one cask of 1400 pounds of thirty-three per cent. bleaching powder in one charge the yield was not less than 200 pounds of chloroform, and about 130 pounds of recovered acetone, thus proving conclusively the gravity of the unaccountable errors of the Siemerling work, and showing a basis for the mischief done by this bad work.

Looking back from this later day at the authoritative way in which these mistakes and misstatements of Siemerling were published and quoted, it is easy to see that nothing could be better adapted to obstruct or prevent any increase in the general production of acetone-chloroform, and to confine its productions to those manufacturers who were using the process secretly.

One of the definite evil consequences of this Siemerling paper was the adoption of its erroneous results as the basis of the following patent.

On June 23, 1886, Gustav Rumpf applied for a patent, and on July 5th, 1888, patent No. 383,992 was issued to him for the invention of "A New and Useful Improvement in the Manufacture of Chloroform from Acetone," of which the following is a specification: "The essential feature of this invention is based on the discovery that acetone when treated in the proper way with a hypochlorite—for example chloride of lime—will yield a larger quantity of chloroform than has been heretofore known. Watts, in his Dictionary of Chemistry, edition of 1883, 1, 918, says that the manufacture of chloroform from acetone cannot usefully be carried out, not only because the price of acetone is too high, but particularly because acetone yields about thirty-three per cent. of its own weight of chloroform when it is treated with chloride of lime. Watts distilled thirty grams of acetone with 150 grams of chloride of lime, and rectified the watery distillate with forty grams of chloride of lime. I have discovered a method whereby it is possible to obtain a yield of chloroform from ace-

tone very much greater than that obtained by Watts. I have found that the reaction may be made to take place in such a way that one equivalent of acetone will yield one equivalent of chloroform by volume, or about 180 per cent. by weight, and the advantages of my invention may be secured in a greater or less degree by properly employing with about fifty-eight pounds of acetone more than 300 pounds of good chloride of lime. The best results and greatest yield of chloroform can, as I have found, be obtained by the use of, say, fifty-eight pounds of acetone to at least 600 pounds of a good chloride of lime containing about thirty-five per cent. of available chlorine, and in proportion if the chloride of lime is poorer. The yield of chloroform will then be from 150 per cent. to 180 per cent. of the weight of the acetone employed instead of about thirty-three per cent.

Then follow claims for invention of diluting the acetone and of introducing it periodically during the process—of introducing it below the surface of the solution in the still—of the use of a mechanical stirrer, and of the use of a still and condenser which are described and figured.

The basis upon which this patent rests, for its reason to be, is the quotation from Watts' Dictionary. Watts quotes the process from *Gmelin's Handbook*, and Gmelin quotes it from *Siemerling's Paper* in the *Archiv der Pharmacie*, 1848, 54, 26. Now, as the paper and quotations are grossly erroneous, and as writers of preceding papers publish results that approximate those of the patent, it might reasonably be asked what is the value of the patent. But the present writer, while intending to make acetone-chloroform, very earnestly desires to avoid all question in regard to the validity of this patent, and therefore uses the Watts (Siemerling) process, which is outside the limit claimed by the patent, with an entirely different apparatus and management described by him in 1857, and republished in *Ephemeris*, 4, [1] 71.

It is proposed to use charges of 280 pounds of absolute acetone to 1,400 pounds of thirty-five per cent. bleaching powder, one to five—to pass the resulting chloroform through scrubbers, then distil it through water, then distil it from a small portion of bleaching powder, then pass it through sulphuric acid scrubbers,



and finally rectify it in three fractions, the large middle fraction being accepted, and the others being worked over.

A part of the great excess of acetone taken in the one to five proportion is recovered by continuing the distillation after the chloroform is all over. Another part is recovered in the wash water from the scrubbers and the distillation, and the small remainder is decomposed by the small proportion of bleaching powder, the total amount recovered being practically not far from the total excess.

To this recovered acetone, carefully assayed, new acetone is added to make up the 280 pounds for the next charge.

The patentees were invited to see this apparatus and process in order to convince them that there is a strong desire to avoid any color of infringement by taking the Siemering proportions which are excluded from their patent. But they took the ground that this was a mere evasion, or getting round their patent by using the excess of acetone over again, and could not be made to see that this, if objectionable, is so by defect in the equity of the patent, and is a proceeding that ante-dated the patent by many years. And finally they covered everything by claiming that the patent secured to them the sole right to make chloroform from acetone in the United States, thus claiming a reaction that had been well known for more than fifty years.

As to the reasons why large manufacturers of chloroform did not avail themselves earlier of the acetone process, the first answer is that it is probable that many of them, in Germany, at least, did so secretly as soon as acetone became cheaper than alcohol.

But, as to other more positive reasons, the writer, as having been for many years a large manufacturer from alcohol, and as having, with all other makers, given up the manufacture rather than contest this patent, can only speak for himself. He for many years doubted the identity of alcohol and acetone-chloroform, and doubted whether the latter was as easily purified for use as the former, so that when chloroform was offered to him at so low a price as to insure that it was made from acetone it was refused. Chloroform has always been a most important agent, and during the earlier part of its career the numer-

ous fatalities from its use were charged to its impurities, so that the alcohol process was adhered to until the identity of the products from alcohol and acetone was fully proved,—not only chemically, but also by surgical experience of considerable duration. Then as time passed and the subject came up for research and reconsideration, the Siemerling results came up also and settled the question against acetone.

Finally Dr. Gustav Rumpf, a German, and an employé for some years in an acetone-chloroform manufactory in Germany, where there is no patent, came to this country, took out these patents and assigned them to the present holders, so that now for the past seven years or more any one making acetone-chloroform in this country by processes that had been free and largely used in Germany for many years, was liable to prosecution for infringement.

Having any general knowledge of the history of acetone and acetone-chloroform, it is difficult to understand how such patents could be issued that would claim to control the proportions of well known chemical materials in long known chemical reactions. But such patents were issued, and, therefore, command respect. That the processes were not used earlier in this country may be charged chiefly to the endorsements of the Siemerling paper; and that the patents appear to have been so long acquiesced in is due to the circumstance that any one who might contest them would do so at great cost of money, time and annoyance in defensive litigation, which, if successful, would secure the benefits equally to many manufacturers, and to the public in lower prices of the products, whilst the contestant would bear all the costs.

In seeking new outlets for acetic acid the writer determined to convert the acid into chloroform, and determined also to respect these patents. In the intermediate step of making acetone, acetic acid was used, not to evade the patents, but because by its use the impurities of the crude acetates of lime were avoided, and a larger yield of better acetone was obtained. In the use of acetic acid instead of the acetates of the patent an entirely different apparatus and management are required and used, and if the patent did not exist the writer would not use either its appa-

ratus or management, but would prefer the rotary still and the continuous process.

With regard to the other step wherein the acetone is converted into chloroform, this is accomplished by a reaction that was long and well known before the date of the patent, and the proper portions of the material required for the reaction were easily obtainable by calculation, and this knowledge also ante-dated the patent. The patent then simply covers a specially devised and described apparatus and management which the writer does not use and does not want to use even if they were not patented, but much prefers his old form of apparatus and management described in 1857, and used for many years in making alcohol chloroform. And the successful use of this apparatus and management for acetone chloroform is simply in accordance with the statement of Liebig, in 1832, that acetone could be successfully used under the same conditions as alcohol.

### PYRIDINE ALKYL HYDROXIDES.<sup>1</sup>

BY A. B. PRESCOTT AND S. H. BAER.

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#### THE HYDROXIDES OF QUATERNARY NITROGEN BASES IN GENERAL.

TETRAMETHYL and tetraethyl ammonium hydroxides were well described by their discoverer, A. W. Hofmann,<sup>2</sup> in 1851. Their crystallization in a vacuum, their behavior as alkalies in reaction with the metallic salts, and their conversion to carbonates upon exposure to the air were then set forth. Various quaternary bases of mixed formation from methyl, ethyl, amyl and phenyl were made by Hofmann at the same time. The tetrapropyl ammonium hydroxide was first described by Roemer, in 1873.<sup>3</sup>

The decomposition of quaternary ammonium hydroxides by heat was reported upon by A. W. Hoffmann, in 1881,<sup>4</sup> also by Lawson and Collie, in 1888.<sup>5</sup>

<sup>1</sup> Read at the Cleveland meeting.

<sup>2</sup> Phil. Trans., 1851, (2), 357; *Ann. Chem.* (Liebig), 81, 253, 86, 292, 91, 33.

<sup>3</sup> H. Roemer, *Ber. d. chem. Ges.*, 6, 786.

<sup>4</sup> *Ber. d. chem. Ges.*, 14, 494.

<sup>5</sup> *J. Chem. Soc.*, 53, 634.

Pyridine ethyl hydroxide was mentioned by Anderson in 1855.<sup>1</sup> The methyl hydroxide was reported upon by A. W. Hofmann in 1881.<sup>2</sup> In this relation are to be considered the numerous products of the action of alkalies upon the alkyl iodides of pyridine and quinoline, obtained by Claus and by Decker, mostly in 1892 and 1893.<sup>3</sup>

#### PYRIDINE PROPYL HYDROXIDE.

Pyridine propyl iodide, prepared as stated in another paper from this laboratory,<sup>4</sup> was treated with moist recent silver oxide, shaking for some time in a flask, keeping down the temperature. The silver oxide for all this work was made by precipitating silver nitrate with potassium hydroxide and washing the precipitate until the washings give no color reaction with hematoxylin, to ensure the removal of the alkali. Silver oxide is sufficiently soluble in water for its solution to color litmus or phenolphthalein.

On filtering out the silver iodide, the solution of pyridine propyl hydroxide was colorless, and was found to precipitate salts of lead, silver, copper, iron, aluminum, chromium, cobalt, and nickel, an excess of the hydroxide dissolving only the precipitates of lead and of aluminum, these reactions agreeing with those of fixed alkalies. In parallel treatment with pyridine it was found not to precipitate these salts, the only apparent reaction with any of them being a blue color with the copper salt. The solution of pyridine propyl hydroxide gave the alkaline reaction with the following indicators: litmus, phenolphthalein, brazil wood, cochineal, hematoxylin, and methyl orange. Pyridine gives an alkaline reaction with all these indicators except phenolphthalein and hematoxylin, these two being capable of use in a volumetric acid estimation of the pyridine propyl hydroxide in presence of pyridine.

On heating the solution of the pyridine propyl hydroxide it acquires a red color, and the solid residue by evaporation has a black color, dissolving in water again as a red solution.

<sup>1</sup> *Ann. Chem. (Liebig)*, 94, 361.

<sup>2</sup> *Ber. d. chem. Ges.*, 14, 1498.

<sup>3</sup> *J. prakt. Chem.* (2), 46, 106, 47, 208, 426; *Ber. d. chem. Ges.*, 25, 3326.

<sup>4</sup> A. B. Prescott, this Journal, 18, 92.

## PYRIDINE ISOPROPYL HYDROXIDE.

This base was prepared in the same manner as the normal propyl hydroxide, and it was found to give the same reactions with indicators and with metallic salts, as well as the same color when evaporated.

The isopropyl<sup>1</sup> base has been elsewhere stated by one of us to form a more stable iodide, of higher melting point and lower solubilities, than the iodide of the normal propyl base, and the isopropyl hydroxide has been taken, instead of the normal propyl hydroxide, in our further experimentation.

The production of the pyridine isopropyl hydroxide, in solution, can be made quantitatively complete as a base saturating sulphuric acid. Weighed portions of the iodide were converted to hydroxide in solution, with due precautions against loss, and the liquid titrated with tenth normal solution of sulphuric acid, using hematoxylin and cochineal, respectively, as indicators, and titrating back to the end reaction with tenth normal solution of potassium hydroxide. The hematoxylin was used in a titration to avoid interference by free pyridine, should this be present as a product of decomposition, as it does not color this indicator. The cochineal was used because it is an indicator of special delicacy for titration of pyridine alkyl hydroxides.

The results were as follows: the percentage of hydroxide *calculated* from the iodide being 55.82, the percentage of hydroxide *found* by titration with cochineal was 55.25 and 55.88, with hematoxylin it was 55.6 and 55.7.

The solution of pyridine isopropyl hydroxide, on evaporation to dryness, yields a black residue, which is permanent, so that after standing three months it gives with metallic salts all the reactions of the hydroxide. The color in solution changes to red, like that of the normal propyl hydroxide. By exposure to the air it is steadily converted to the carbonate.

When the solution was treated for some time with carbon dioxide gas, then evaporated to dryness, the residue was found to bear the composition of a normal carbonate of the univalent base. This composition was determined from the amount

<sup>1</sup> Pyridine Alkyl Iodides, this Journal, 18, 93.

of carbon dioxide recovered in an absorption train, in ratio to the weight of iodide taken for conversion to hydroxide. The calculated weight of carbon dioxide being 14.44 per cent. of  $(C_5H_5N.C_3H_7)_2CO_2$ , there were obtained 14.99, 14.88, and 14.79 per cent. of carbon dioxide. In other trials the carbonation was incomplete, reaching only to 9.3, 9.47, and 10.1 per cent.

In no case was the full quantity of pyridine isopropyl hydroxide obtained in weight of the dry residue, although the evaporation was conducted under different conditions, in vacuum, in a stream of dry air, and in a stream of dry hydrogen. In the case of the carbonate, the weight of the residue did not fall below the theoretical quantity. As hydroxide the weight of the residue always fell a good deal short of the full quantity.

Pyridine isopropyl platinum chloride, perfect in proportions, was prepared from the black residue left on evaporation of the water solution of pyridine isopropyl hydroxide, by treatment in the usual manner. The black mass was dissolved in alcohol, treated with hydrochloric acid and platinum tetrachloride, and the crystalline precipitate fitted for analysis. Fine crystals were obtained, not melting below temperatures which cause decomposition.

	Calculated for $(C_5H_5N.C_3H_7Cl)_2PtCl_4$ .	I.	Found. II.	III.
Platinum. ....	29.95	30.08	30.48	30.29
Chlorine .....	32.58	32.50	....	32.39
Ratio of Cl to Pt.....	100:108	100:108	....	100:107

Pyridine isopropyl sulphate, the normal salt, was also prepared in fine crystals, by adding sulphuric acid to the hydroxide.

In various efforts to obtain the pure hydroxide in the solid state, crystalline or amorphous, vacuum desiccation, freezing temperatures, formation in absolute alcohol solution, and other agencies were successively tried, without success. Crystals were not obtained, and the residue was always dark colored. Evaporation in a stream of dry hydrogen yielded a residue of the same weight as that obtained by evaporation in a stream of dry air.

These results, so far, may be summarized as follows :

Pyridine isopropyl hydroxide remains in aqueous solution for

a time without decomposition or loss in any way. The residue by evaporation of this solution, in air, or hydrogen, or vacuum, contains a considerable portion of the unchanged hydroxide, along with certain decomposition products not yet determined. The normal carbonate of this base, its normal sulphate, and its platinum chloride are easily prepared and preserved.

UNIVERSITY OF MICHIGAN.

### ON THE REDUCTION OF SULPHURIC ACID BY COPPER, AS A FUNCTION OF THE TEMPERATURE.<sup>1</sup>

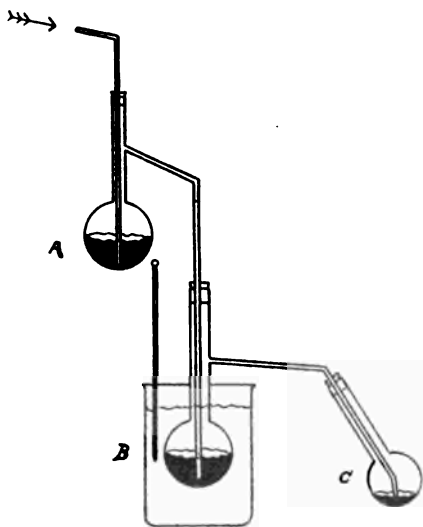
BY LAUNCELOT ANDREWS.

Received January 9, 1896.

THE object of the experiments described in this paper was to determine whether the reduction of sulphuric to sulphurous acid by copper take place at a higher or a lower temperature than the incipient dissociation of the former compound into water and the acid anhydride.

The sulphuric acid employed was the ordinary pure product, containing 98.4 per cent. of sulphuric acid. The apparatus illustrated in the adjoining figure was used.

The method resorted to was to heat the copper with the sulphuric acid (in flask *B*) gradually in a sulphuric acid bath, while passing a dry current of air or of carbon dioxide through it. The escaping gas was then tested (in flask *C*) by suitable reagents, to be described, for sulphuric and sulphurous acids respectively. Flask *A* contained concentrated sulphuric acid at the ordinary temperature (25° C.) to dry the gas, which was passed at the rate of about eighty bubbles per minute, except when otherwise men-



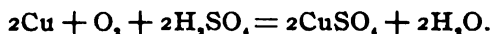
<sup>1</sup> Read before the Iowa Academy of Sciences, January 2, 1896.

tioned. The importance of securing absence of dust being recognized, the whole interior of the apparatus was washed with boiling concentrated sulphuric acid, then with water and dried in dustless air.

*Experiment I.*—Flasks *A* and *B* were charged with concentrated sulphuric acid and *C* with a solution of barium chloride. Air was drawn through the whole in a slow current for fifteen minutes. The solution *C* remained clear. *B* was now very slowly heated, while the current of air was maintained. Before the bath reached 70° C. there appeared in *C* a faint turbidity of barium sulphate which, at the temperature named, became distinct, but at 60° C. the solution remained unchanged even after passing the air for a long time. Hence, sulphuric acid of the given concentration begins to give up sulphur trioxide, that is, it begins to dissociate at a temperature lying between 60° and 70° C. and nearer to the latter.

*Experiment II.*—The apparatus was charged as before, with the addition of pure bright copper wire in *B* and with highly dilute iodide of starch in *C* instead of barium chloride. After passing air for several hours at the ordinary temperature, much of the copper had gone into solution and anhydrous copper sulphate had crystallized out, but the iodide of starch, made originally very pale blue, retained its color.

This shows that in the presence of air sulphuric acid is attacked by copper at ordinary temperatures, but without reduction of the acid. The reaction must take place in accordance with the equation,



*Experiment III.*—This was like the last, except that the apparatus was filled with carbon dioxide<sup>1</sup> and a current of this gas was substituted for air. The copper was not attacked and the starch iodide was not decolorized. The temperature of *B* was now slowly raised, and when it reached 90° C. the solution in *C* was bleached.

In a similar experiment a solution of dilute sulphuric acid colored pale straw yellow with potassium bichromate was used as an indicator for sulphurous acid in *C*. In this case the change

<sup>1</sup> Freed from oxygen by bubbling through chromous acetate.



of color did not occur until the temperature had risen to  $108^{\circ}\text{C}.$ , the indicator being, as might be expected, less sensitive than the other.

*Experiment IV.*—This resembled III, except that a reagent for both sulphuric and sulphurous acid was used in *C*. This reagent was prepared by slightly acidifying a semi-normal solution of barium chloride with hydrochloric acid and then adding enough potassium permanganate to render the solution pale rose color. This indicator is capable of showing the presence of considerably less than 0.01 milligram of sulphurous acid.

When the temperature of the bath had reached  $70^{\circ}\text{C}.$  the solution in *C* was distinctly turbid with barium sulphate, but its color was unaltered. At  $86^{\circ}$  it began rather suddenly to bleach, and at  $87^{\circ}$  it was colorless. Special care was taken in filling *B* not to get any sulphuric acid on the neck or sides of the flask. A repetition of this experiment gave identical results, the gas being passed at the rate of two or three bubbles per second.

The conclusions to be drawn from this investigation are :

First. That the dissociation<sup>1</sup> of sulphuric acid of 98.4 per cent. begins to be appreciable at a temperature somewhat below  $70^{\circ}$ , which may be estimated at  $67^{\circ}\text{C}.$

Second. The reduction of sulphuric acid by copper does not begin below  $86^{\circ}$ , that is not until the acid contains free anhydride.

The assertion made by Baskerville<sup>2</sup> that sulphuric acid is reduced by copper at  $0^{\circ}$  is, therefore, incorrect. He appears to have based the statement, not on any demonstration of the formation of sulphurous acid, but solely on the formation of copper sulphate, which occurs as I have shown<sup>3</sup> in consequence of the presence of air. I believe that a repetition of his experiments under conditions securing entire absence of oxygen can but lead him to a conclusion different from that to which he now adheres.

<sup>1</sup> The appearance of barium sulphate in *C* can not be accounted for by an assumed volatility of sulphuric acid as such, but only by its dissociation, because volatilized sulphuric acid would condense in the cold tube between *B* and *C*, since it has been shown that the acid was not appreciably volatile at the temperature of the latter. Hence only the anhydride could pass this cold tube and appear as sulphuric acid in *C*.

<sup>2</sup> This Journal, 17, 908.

<sup>3</sup> Traube has shown the same thing for dilute sulphuric acid. *Ber. d. chem. Ges.*, 18, 1868.

The fact adduced by him that, under certain conditions, cuprous sulphide may be formed by the action of the metal upon sulphuric acid does not allow any conclusions to be drawn respecting the presence of "nascent" hydrogen, since it may be explained perfectly well, either by the direct reducing action of the copper or by Traube's theory, which is backed up by *almost* convincing evidence.<sup>1</sup>

Stannous chloride will reduce sulphuric acid with formation of hydrogen sulphide, sulphurous acid and free sulphur: an analogous reaction in which the assumption of "nascent" hydrogen is inadmissible.

I hope to complete before long another series of experiments, now under way, which will form in a future communication a further contribution to the subject of the present paper.

### THE OXIDATION OF SILVER.

BY CHARLES E. WAIT.

Received January 17, 1896.

**I**N a former paper<sup>2</sup> I had occasion to call attention to the large amount of silver present in a sample of bismuth litharge from a western smelting and refining company. The silver in this instance estimated in the metallic state was 2.94 per cent.

There was some doubt expressed as to the condition in which the silver existed, it being usually reported in the metallic state. Upon investigation it was found, as was shown in the paper referred to, that the silver did not exist wholly in the metallic state, but partly in another form, probably the oxide.

The conclusions reached at that time were based upon the following experiments:

1. A weighed sample of the litharge was boiled in acetic acid for about half an hour, the solution was filtered, and the filtrate gave no reaction for silver.

2. Same as above, but with continued boiling, the filtrate gave no reaction for silver.

3. A sample was placed in cold acetic acid, kept there for half an hour, then heated to boiling, the solution was filtered, the lead was precipitated, and in the filtrate silver was found to exist, corresponding to 19.25 per cent. of the silver in the litharge. Other determinations gave closely agreeing results, and

<sup>1</sup> Moritz Traube, *loc. cit.* and *Ber. d. chem. Ges.*, 18, 1877.

<sup>2</sup> Trans. Am. Inst. Min. Eng., 15.

it is interesting to note that the residues contained grains of metallic lead, or argentiferous lead.

I have placed the following interpretations upon the above results:

In Nos. 1 and 2 if any silver in any form was dissolved in the acetic acid, it was in turn reprecipitated by boiling, in the presence of metallic lead.

In No. 3 the silver dissolved, did not in all probability exist in the metallic state; and in this case was not precipitated by the lead, or argentiferous lead, the solution being brought merely to the boiling temperature.

I have been led to the above interpretations by showing that neither metallic silver reduced to fine subdivision by mechanical means, nor silver freshly prepared by zinc from silver chloride is soluble in acetic acid, while argentic oxide is soluble in that acid; and a solution of silver oxide in acetic acid was precipitated completely by metallic lead upon boiling.

If the oxides are decomposed at a temperature of  $300^{\circ}$  C.,<sup>1</sup> or less,<sup>2</sup> how may we account for the existence of this substance in a product so highly heated as the litharge from the refining furnace?

Berthier<sup>3</sup> has observed that lead may be oxidized by oxide of copper, when melted together, and further consideration of the subject shows that certain metals may be oxidized by being melted with an oxide of another metal, this oxidation depending in all probability upon the excess of the oxide present. Silver does not appear to be oxidized by oxide of copper if the results in experiment No. 18 are trustworthy.

According to Fournet's experiments<sup>4</sup> silver is not an exception to the metals to which litharge gives up a part of its oxygen when fused with them for a considerable time.

While it is true that in the process of cupellation there is a loss of silver due possibly to oxidation, yet I do not find any losses even in the most exaggerated cases at all comparable with the percentages of silver oxide which I have been able to produce by a simple, yet possibly new, method.

It seemed to me an interesting problem to ascertain, if possible, the conditions under which silver may be oxidized at a high

<sup>1</sup> Roscoe and Schorlemmer, Vol. II, Part I.

<sup>2</sup> *J. Chem. Soc.*, 65, 316.

<sup>3</sup> Crookes and Rohrig, *Metallurgy*.

<sup>4</sup> Erdman's *Journal*.

temperature, and the conditions under which the oxide of silver, if thus formed, would remain as such.

Some interesting work has been done along a similar line,<sup>1</sup> that is, a study of those oxides which are stable at high temperature, and those which are decomposed, but under neither head does silver seem to have been discussed.

So few observations have been made along this exact line, as far as I have seen, that I have been induced to make some investigations with a view to throw light upon the subject, if possible.

The general method of conducting the experiments, I will briefly state as follows: Metallic silver in minute subdivision was incorporated with one of the several bodies mentioned below, this mixture was put in a cupel of bone ash, or in a scorifier, and then placed in the muffle of an assay furnace and subjected to an oxidizing heat.

After this operation the mass was removed to a mortar, pulverized, then digested with acetic acid to boiling, the solution was filtered; in case a lead compound had been used, the lead was removed by sulphuric acid, hydrochloric acid was then added. The silver chloride thus formed was filtered, dried, and wrapped in least pure lead foil and then carefully cupelled.

There was thus obtained the silver, which was converted to argentic oxide,—at least I assume it to be such,—and it is interesting to note that the amount of silver converted to oxide, and tabulated below, shows a very great range, in fact from only a trace to as much as thirty-nine per cent. of the silver used.

This variation seems dependent upon a number of conditions, namely: the body with which the silver was mixed, duration and condition of heat, whether low, medium, or high temperature. As I did not use a pyrometer to ascertain the temperature during these experiments, I have thought it desirable to indicate the degree of heat approximately by such terms as "low," "medium," and "high," referring to the condition of the heat as usually obtained in the muffle in the assay of silver.

I append herewith several tables of experiments and results:

<sup>1</sup> *J. Chem. Soc.*, April, 1894.

TABLE A.

No. ex- periment.	Ag in gram.	Heated with.	Time of heat.	Condition of heat.	Per cent. Ag. as Ag <sub>2</sub> O.
1	0.5	2.5 grams MnO <sub>2</sub> .	60 min.	medium	9.40
2	0.5	5.0 " MnO <sub>2</sub> .	60 "	"	7.78
3	0.5	2.5 " Fe <sub>2</sub> O <sub>3</sub> .	60 "	"	none.
4	0.5	2.5 " Bi <sub>2</sub> O <sub>3</sub> .	60 "	"	"
5	0.5	2.5 " ZnO.	60 "	"	"
6	0.5	2.5 " CaCO <sub>3</sub> .	60 "	"	"

From the above it will be seen that silver oxide was produced, and remained as such where manganese dioxide was used and in no other case; it would also seem that this oxide was made at the expense of the manganese dioxide and not by atmospheric oxidation, nor does it seem to have been produced in experiment 3, (certainly not remaining as such) assuming the possible conversion of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>.<sup>1</sup>

TABLE B.

No. ex- periment.	Ag. in gram.	Heated with.	Time of heat.	Condition of heat.	Per cent. Ag. as Ag <sub>2</sub> O.
7	0.5	7.5 grams MnO <sub>2</sub> .	30 min.	medium.	34.16
8	0.5	10.0 " MnO <sub>2</sub> .	30 "	"	18.84
9	0.5	3.0 " CaCO <sub>3</sub> .	60 "	"	none.
10	0.5	3.0 " Fe	60 "	"	"

The above results show that silver oxide was produced in the presence of manganese dioxide only; that less duration of heat than in Table A gives the amazingly large per cent. of that oxide, and it furthermore seems that the oxide produced is not in proportion to the manganese dioxide used, but the reverse condition is generally seen in each set of experiments.

TABLE C.

No. ex- periment.	Ag. in gram.	Heated with.	Time of heat.	Condition of heat.	Per cent. Ag. as Ag <sub>2</sub> O.
11	0.5	1 gram MnO <sub>2</sub> .	2.5 min.	high.	32.24
12	0.5	2 grams MnO <sub>2</sub> .	2.5 "	"	34.28
13	0.5	2 " MnO <sub>2</sub> .	20 "	"	11.72

The above experiments show, other conditions being the same, the longer the duration of the heat the less oxide there is produced.

<sup>1</sup> *J. Chem. Soc.*, 65, 313.

TABLE D.

No. ex- periment.	Ag. in gram.	Heated with.	Time of heat.	Condition of heat.	Per cent. Ag. as Ag <sub>2</sub> O.
14	0.5	5 grams PbO.	10 min.	medium.	38.85
15	0.5	4 " PbO <sub>2</sub> .	10 "	"	35.12
16	0.5	2 " BaO <sub>2</sub> .	5 "	"	12.28
17	0.5	7 " BaO <sub>2</sub> .	10 "	high.	2.04
18	0.5	4 " CuO.	12 "	"	none.

In Nos. 14 and 15 the mixtures were placed in scorifiers, and covered with ten grams of lead oxide.

In Nos. 16 and 17 the mixtures were placed in cupels and covered with two grams of barium dioxide.

It is interesting here to notice that barium dioxide serves as an oxidizing agent; that the amount of silver oxide produced decreases probably both with increase of time and temperature.

Although lead dioxide may readily give up a part of its oxygen and thereby be converted into a lower oxide, yet the amount of silver oxide produced was no greater than with lead oxide alone; this is an interesting illustration of the property of lead oxide to serve as a possible carrier of atmospheric oxygen, producing silver oxide in a manner similar to that of the two bodies, manganese dioxide and barium dioxide, liberating oxygen. In the case of lead oxide, No. 14, if dissociation is not possible<sup>1</sup> even at so high a temperature as 1750° C, it seems most reasonable to account for its peculiar oxidizing action, as mentioned above; *viz.*, as a carrier of atmospheric oxygen. Although copper oxide has been shown to yield up a part of its oxygen at 1500° C, yet I find no evidence of silver oxide existing in experiment 18 in the remaining ignited mass.

TABLE E.

No. ex- periment.	Ag <sub>2</sub> O. in gram.	Heated with.	Time of heat.	Condition of heat.	Per cent. Ag. as Ag <sub>2</sub> O.
19	0.5 Ag <sub>2</sub> O.	5 grams MnO <sub>2</sub> .	60 min.	medium.	36.4
20	0.5 Ag <sub>2</sub> O.	3 " Fe.	60 "	"	0.3
21	0.5 Ag <sub>2</sub> O.	3 " CaCO <sub>3</sub> .	30 "	"	0.2

In Table E a variation was made in the nature of the experiment. Freshly prepared silver oxide was used; while this oxide was completely decomposed upon being heated gently upon a porcelain lid, yet in No. 19 where manganese dioxide

<sup>1</sup> *J. Chem. Soc.*, 65, 316.

was used, it will be seen that 36.4 per cent. of this silver oxide completely escaped decomposition.

The above results, in connection with others along a similar line, have induced me to believe that attention has not heretofore been directed to the ease with which silver may be oxidized by lead oxide, and particularly by substances which give up a part of their oxygen upon gentle ignition, such as manganese dioxide and barium dioxide. Is it not then reasonable to assume that certain losses, or irregularities in the treatment of silver and its compounds, may be due to this cause?

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### THE DETERMINATION OF THE SOLID FAT IN ARTIFICIAL MIXTURES OF VEGETABLE AND ANIMAL FATS AND OILS.

BY J. H. WAINWRIGHT.

Received February 1, 1896.

It will readily be conceded by most analysts that there is no subject in analytical chemistry presenting more difficulties than the examination and analysis of the fixed oils and fats. This is especially true in the case of mixtures of oils of different origin, and there is probably no problem more difficult to solve in most cases than the analysis of such a mixture when even approximately correct quantitative results are required.

It is only within a comparatively recent period that the investigations of the chemist have been especially directed to this branch of research as formerly the character and identity of a sample of unknown origin was chiefly, but very doubtfully, established by means of obscure color reactions and one or two simple determinations, such as specific gravity, melting point, etc.

At present, however, the investigations of many learned chemists have shown that determinations of the chemical and physical properties of a sample, such for example as the combining weight of fatty acids, the percentage of iodine the sample will absorb, the percentage of volatile fatty acids, etc., will yield results by which may be established, in most cases with reasonable accuracy, the fact as to whether it is a simple oil or fat, such as olive, linseed, lard, butter, etc., and if so its iden-

tity and quality; or, if adulterated, to determine with a fair degree of accuracy the character and probable extent of adulteration. This is especially the case when a mixture consists of but two oils or fats, one of which is known, in which case a few quantitative determinations will usually enable the analyst to readily ascertain its approximate composition.

If a sample, however, consists of a mixture of *more* than two oils or fats, any statement of its composition calculated from the results of such determinations as above mentioned would be of extremely doubtful accuracy in any case, even if one of the constituents were known, and even then it would be at best but a broad approximation owing to the variations in chemical and physical properties exhibited in different specimens of the same kind of oil.

Some years ago samples of compound lard for export were submitted to the United States Laboratory for analysis with a view to determining the relative proportions of its constituents in order that the claim of the exporter for "drawback" of duties paid on one of its constituents might be verified.

This "compound lard" or "lard compound" has in recent years become an important article of commerce and consists essentially of cotton-seed oil and oleostearin made from beef fat mixed in different proportions; and sometimes containing a small percentage of genuine lard. Its composition is variable according to the brand and particular formula by which compounded, but is generally about as follows:

	Per cent.
Oleostearin .....	20 to 30
Cottonseed oil .....	70 to 80
or	
Oleostearin .....	18 to 30
Lard .....	10 to 20
Cottonseed oil .....	65 to 75

In the first case determinations of the properties of the sample would disclose its composition with reasonable accuracy, but in the second case considerable time was spent, I might almost say wasted, in making a long series of these determinations, both on the samples themselves and on mixtures made in the labora-



tory in accordance with the formula for comparison, without arriving at any satisfactory conclusions, until finally a very simple method for the analysis or rather assay of these "lard compounds" was devised, which up to the present time seems to yield fairly satisfactory results.

About 150 grams of the sample is placed in a beaker and heated in a boiling water bath until entirely melted. The water is kept boiling for at least one hour and is then allowed to cool gradually without removing the beaker from the bath until the temperature is reduced to about 75°-80° F. It is then allowed to stand for at least twelve hours in a moderately warm place.

In practice the beaker immersed in the warm water of the bath is left standing in the laboratory over night at the ordinary room temperature which is usually all that is necessary excepting in very warm weather when the temperature should be reduced by artificial cooling.

This process causes the solid fat to crystallize, which being accomplished, fifty grams of the sample is weighed from the beaker after its contents have been thoroughly mixed by means of a glass rod or spatula, and is carefully wrapped in a double thickness of Canton flannel in which it is subjected to pressure in a small screw press.

The pressure should be applied very gradually, especially at first, and should be continued until the screw has been forced down as tightly as possible. After standing a few minutes to permit the oil to drain off, the contents of the press are removed and the cake of solid fat, consisting essentially of stearin, is easily separated from the cloth in which it is wrapped and can then be weighed.

The press used is called "Osborne's Patent Beef Press," and can be obtained in almost any hardware store, and is used for domestic purposes, such as the preparation of "beef tea," etc.

The length of time required is usually at least one hour, and the temperature seems to be a matter of comparative indifference provided, of course, extremes are avoided.

No great accuracy is claimed for this method, and that it is based on any thing like *strictly* scientific principles remains to

be proved, but the following results will, I think, show that it is what it is claimed to be, *i. e.*, a useful, if rough method for the assay of these manufactured compounds, and it is especially valuable as a preliminary operation in the more extended process of analysis.

Mixtures of the various ingredients, *i. e.*, oleostearin, lard and refined cottonseed oil were made in the laboratory, of which the following, as well as many others, are typical examples :

No. 1.		Grams.
Oleostearin .....		20
Lard .....		10
Cottonseed oil .....		70
No. 2.		
Oleostearin .....		25
Lard .....		10
Cottonseed oil .....		65
No. 3.		
Oleostearin .....		25
Cottonseed oil .....		75
No. 4.		
Oleostearin .....		24
Lard .....		10
Cottonseed oil .....		66

which, when assayed by the above described method, yielded respectively :

Number.	Per cent.
1.....	19.6
2.....	25.2
3.....	25.8
4.....	25.2

The following are the results obtained with samples of different formulas submitted for analysis :

SAMPLE A.		Per cent.
Oleostearin .....		30
Cottonseed oil .....		70
SAMPLE B.		
Oleostearin .....		25
Lard .....		10
Cottonseed oil .....		65

## SAMPLE C.

Oleostearin .....	25
Cottonseed oil .....	75

## SAMPLE D.

Oleostearin .....	25
Lard .....	10
Cottonseed oil .....	75

## SAMPLE E.

Oleostearin .....	25
Cottonseed oil .....	75

## SAMPLE F.

Oleostearin .....	23
Lard .....	10
Cottonseed oil .....	67

## SAMPLE G.

Oleostearin .....	23
Lard .....	10
Cottonseed oil .....	67

## SAMPLE H.

Oleostearin .....	34
Lard .....	10
Cottonseed oil .....	68

## SAMPLE I.

Oleostearin .....	25
Cottonseed oil .....	75

which, upon assay as above, gave the following percentages, respectively :

	Per cent.
A .....	29.2
B .....	26.4
C .....	24.4
D .....	26.2
E .....	25.2
F .....	24.6
G .....	23.9
H .....	24.4
I .....	24.5

All of the above assays would seem to show that the results yielded are correct to within about one and a half per cent., and in my opinion it would be perfectly safe to consider that as a reasonable margin of error.

In consideration, however, of the character of the process of

assay as well as the character of the mixture and of the samples analyzed, I do not believe the analyst would be justified in reporting any *exact* amount of oleostearin found and have therefore adopted the form of reporting that the sample submitted contained "not less than — per cent., nor more than — per cent.," the margin of the error being as stated.

UNITED STATES LABORATORY.

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## THE MEASUREMENT OF THE COLORS OF NATURAL WATERS.

BY ALLEN HAZEN.

Received January 30, 1896.

THE diffusion of more accurate information and more rational theories as to the causation of diseases during the past few years has resulted in simplifying and changing many of the problems presented in connection with the chemical analysis of public water supplies. The healthfulness of a water for such use is determined to a much greater extent than formerly, by critical inspections of the sources of supply, particularly in the case of surface waters; and information as to the size of the water shed, flow at different seasons, amount of storage and character of the storage reservoirs, together with full information in regard to the population on the water shed and the way it disposes of its sewage, are more important and frequently adequate in themselves to determine the wholesomeness or unwholesomeness of a water; and the use of chemical analysis in connection with the investigation of such problems is rather in serving as an index of the varying amounts of contamination at different times, than in showing the presence or absence of substances which are in themselves injurious to health. Bacterial examinations also, which have become so frequent and necessary in connection with analyses of this character, play also their part in measuring such fluctuations.

There are, however, several determinations which indicate in themselves substances desirable or undesirable in a public water supply, and among these perhaps the most important are the hardness, the color, and in the case of ground water supplies, the iron; and although the color is determined mainly for its own

sake, and because a colorless water is more desirable than a colored water, and not because of any direct relations that the results obtained may bear to the wholesomeness of the supply, the interest that attaches to the determination often makes it of no less importance than those of the ammonia or other organic constituents.

The importance of this question of color has long been felt, and numerous efforts have been made to devise means for measuring and recording the colors. The essential requirements of such a method are that the figures obtained for a given color shall be the same at all times and in all places, and that it shall be possible to reproduce the colors with certainty at any future time. It is also desirable that the figures obtained shall be as nearly as possible proportional to the actual apparent colors of the various waters, as seen under ordinary conditions.

Perhaps the simplest method of measuring the colors of waters consists in taking a solution with a color of substantially the same hue as the waters to be examined, and diluting it with various quantities of distilled water, producing a series of colors with which the waters may be compared and results of relative colors obtained. The most natural substance to use for the colored solution is a highly colored swamp water, but the results obtained with such a standard of color, although comparable among themselves, would hardly have further permanent value owing to uncertainty as to the color of the water used for comparison, and the certainty that this color would fade, and the impossibility of reproducing it with accuracy at a future time. It is evident that any such procedure cannot fairly be considered as establishing a standard of color, and that the colors must have some definite physical basis which can be formulated and described with certainty and which will allow them to be reproduced at pleasure.

Perhaps an ideal basis of description of color would be a statement of the changes in the numbers and intensities of the vibrations in white light produced by passing through a layer of the water under examination. These changes are, however, so hopelessly complex as to defy even the hope of ascertaining them, and even if they could be determined it is doubtful if a statement of them could be made simple enough to convey any

meaning to the ordinary mind as to the colors represented.

The most satisfactory standard which we can reasonably hope to realize is probably furnished by some other substance with a definite color, which can be produced at will, and which can be compared with the colors of waters, furnishing results of permanent value. One of the first attempts at such a standard was made by Messrs. Crooks, Odling, and the late Dr. Tidy,<sup>1</sup> who used solutions of ferric and copper salts in solution in independent vessels, which, superimposed upon each other, produced a color equivalent to that of the water. The fatal objection to this standard was that the color of the iron solution depends very largely upon the formation of basic compounds which vary in the intensity of their colors with very slight variations in acidity and with changes in temperature, so that the results obtained are open to a most objectionable uncertainty.

Another, and in some respects more satisfactory, attempt in establishing a standard was made by Prof. A. R. Leeds,<sup>2</sup> who suggested that extremely dilute solutions of ammonia after being nesslerized should be taken as the standards of color, the quantity of ammonia being taken as an index of the color produced. This standard was certainly most convenient, as the nesslerized ammonia standards are always present in laboratories for water analysis being required for another purpose, and it was believed that the colors had a sufficiently definite value to form a reliable standard.

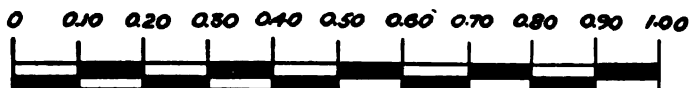
This method has been widely used in the United States, and was employed by the author for several years and for the examination of some thousands of samples of water, until it became apparent that the variations and discrepancies in the results obtained were so great as to require serious consideration. As a result, a critical examination of the colors produced in this way was undertaken with the aid of my then assistant, Mr. Harry W. Clark, the results of which were published in full in the *American Chemical Journal*, 14, 300. It was found in the course of the investigation that the colors produced depended not only upon the amount of ammonia used, but also upon a

<sup>1</sup> *Chem. News*, 43, 174.

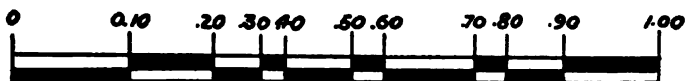
<sup>2</sup> *Proc. Am. Chem. Soc.* 2, 8.

whole series of conditions, many of which were not capable of exact control, so that the results obtained varied among themselves, even in the same laboratory at different times, to a most unsatisfactory extent. It was found that the colors produced depended not only upon the composition of the Nessler reagent and the quantity used, but even upon the way in which it was applied to the water containing the ammonia, and to a very

**UNIFORM SCALE.**



**NATURAL WATER OR NESSLERIZED-AMMONIA SCALES.**



**Irregularities in Nesslerized Ammonia and Natural Water Standards: From Report by Mr. FITZGERALD and Mr. FOSS in Report of BOSTON WATER BOARD for 1893.**

large extent upon the temperature at which the experiment was made. It was further found that the colors produced were not at all proportional to the quantities of ammonia present, even under the most favorable conditions, owing in part to the very considerable color of the Nessler reagent itself, and in part to the fact that small amounts of ammonia produce less color relatively than larger quantities; and as a result of the combination of these two causes the colors increase in an irregular way that is most unsatisfactory. This irregularity of increase is well shown by a cut here reproduced from the report of Mr. FitzGer-

ald and Mr. Foss in the report of the Boston Water Board for 1893,<sup>1</sup> showing the colors of nesslerized ammonia and natural water standards received from the Institute of Technology when read against a single natural water standard in an ingenious colorimeter devised by the authors, and in addition the difference between the two lower scales shows how the standard differed at two different times.

The nesslerized ammonia standard has been improved in an important way by Mrs. Ellen H. Richards, of the Massachusetts Institute of Technology, who has for some years used standards of natural waters diluted with distilled water, as suggested above, and diluted to such an extent as to correspond with the nesslerized ammonia standards at a number of selected points, and with intermediate and lower standards prepared by interpolation between the selected points of comparison. This method of procedure eliminates to a certain extent the daily fluctuations in the values of the nesslerized ammonia standards, and also tends to smooth out the smaller irregularities in the scale, although the larger ones could hardly be removed without destroying the integrity of the scale itself. The method of procedure is, moreover, open to the more serious objections to the nesslerized ammonia standard in that the standards themselves depend for their original values upon the nesslerized ammonia standards of which the exact values are always open to question.

In a recent article published in the present volume of this Journal, page 68, by Ellen H. Richards and J. W. Ellms, an account is given of an attempt to establish in a more accurate and permanent manner the value of the standards used by comparing them with the Lovibond "Tintometer." This instrument consists essentially of a series of colored glasses which are superimposed upon each other to produce a color equivalent to that of a given sample of water or other substance. The tintometer in its construction and operation is so complicated as to render it impracticable, as Mrs. Richards states, to use it for the direct determination of colors in waters where many samples have to be examined, and its use is thus limited to determining

*Franklin Institute, 1898, 401.*



from time to time the values of the standards actually used for measuring the colors which would otherwise be subject to uncontrolled variations.

Several objections may be raised to the use of the Lovibond Tintometer as an ultimate standard of color. If we admit that the colors of the glass slips are permanent and will forever hold their color, we still depend upon the honesty and skill of the manufacturer of the instruments to produce glass slips of precisely the same values as those used in the original apparatus. It is of course conceivable that an apparatus should be continued in use with the same slips for many years, but eventually the slips would become worn or scratched and would require to be replaced, or the apparatus might be destroyed by fire or other accident; and in any case other laboratories buying new instruments will require to have new slips. It is thus seen that the values of the colors depend ultimately upon the honesty and skill of the manufacturer in preserving and reproducing an arbitrary standard, and not upon natural units.

It may be said as against this view that the values of the Lovibond units have been determined by comparison with the colors of solutions of definite chemical composition with such care and precision that it will be possible at future times to determine whether the slips then in use are really the equivalents of those now sold, and that it would even be possible to reproduce them in case the present standards were lost or destroyed. But against this statement it may be urged that it is much more rational, simpler, and better in every way to compare the waters directly with the chemical solutions which are the ultimate points of reference without the intervention of glass slips or other standards.

An attempt to do this was made by the author, who published<sup>1</sup> a description of a method of comparing the colors of waters with those of solutions of platinum and cobalt of known strength, the colors of which were absolutely definite and permanent, and capable of being reproduced with precision at any time, and not affected by temperature or other conditions likely to occur in well regulated laboratories. The method of stating the results

<sup>1</sup> *Am. Chem. J.*, 14, 300.

was a natural and simple one, namely, "that the color of a water is the amount of platinum, in parts per ten thousand which, in acid solution, with so much cobalt as will match the hue, produces an equal color in distilled water."

Since the publication of this article the platinum standard has been used in laboratories under my direction, and by my successors, and in other and independent laboratories for the measurement of colors in many thousands of samples of water, and with such uniformly satisfactory results<sup>1</sup> that I believe it only fair to say a word in regard to the objections raised to the standard by Mrs. Richards in the above mentioned article.

The first of these objections is that there is an excess of orange to yellow in the standard, which, if I understand the language correctly, means that the standard is redder than the waters to be examined. This contingency was provided for in the original article by making the platinum the standard of color and allowing the cobalt to be varied as required to match the hues of the waters. The quantity of cobalt in proportion to the platinum which I suggested, namely, one-half as much metallic cobalt as platinum, was the result of my experience of thousands of samples of water prior to the publication of that article, but as waters from different sources vary in their hues, it was fully recognized that it might be desirable in other cases to use a different proportion of cobalt from that suggested; and if it is found that the quantity of cobalt suggested produces a standard too red for a given set of waters, it is only necessary to make a fresh standard with a somewhat smaller quantity of cobalt to be determined by experiment, when it will be found that the hue matches the waters as closely as it is possible for any single standard to do.

As a matter of fact, standards containing a quarter less and others containing a quarter more cobalt than the amount suggested have been repeatedly used by the author and by others for special purposes, and, while the hues of some waters are more accurately matched, the results as a whole have hardly warranted any change in the proportion suggested for ordinary practical work.

<sup>1</sup> Report of Boston Water Board, 1893, p. 85. Report of Massachusetts State Board of Health on Metropolitan Water Supply, 1895, p. 177. *J. Franklin Institute*, 138, 403.

The second objection is that the standard is not suitable for the measurement of the deeper colors. This is indeed an important question, and had been thoroughly canvassed by the author and his assistants before the publication of the process, and the means for avoiding difficulties from this source were distinctly stated in the article, although the reasons for the precautions to be taken were not perhaps stated as fully as was desirable.

One of the first facts to be learned by persons studying the colors of solutions is that solutions having the same color in one depth or dilution are not necessarily of the same color in greater or less depths or dilutions. The truth of this statement was most strikingly shown in an article published by the author, in connection with Mr. Harry W. Clark<sup>1</sup> in connection with the colors of the various nitrophenols in various dilutions, in which it was shown, for example, that alkaline solutions of ortho- and paranitrophenols are of about the same color when solutions containing one-tenth or a part in a million of nitrogen are seen in depths of 200 mm., while with more dilute solutions the para is more highly colored, and with more concentrated solutions the ortho has the deeper color, and the variations are so astonishingly great that with the most concentrated solutions examined the ortho produced as much color as more than thirty times its weight of paranitrophenol.

The explanation of this remarkable phenomenon has been clearly given by Mr. Desmond FitzGerald and Mr. William E. Foss, in the annual report of the Boston Water Department for 1893.<sup>2</sup> It is there stated that the amount of light which passes through successive equal layers of an absorbing solution diminishes in geometrical progression as the number of layers increases in arithmetical progression; and as the coefficient of transmission varies with different solutions, it often happens that a water matches the standard very closely in hue in a short depth, but appears of quite a different hue in a greater depth. That is to say, taking an extreme case, the coloring-matter in one solution, owing to its chemical or physical properties, absorbs a large percentage of the light from a narrow band of the spectrum,

<sup>1</sup>*J. Anal. Appl. Chem.*, 5, 301.

<sup>2</sup>*J. Franklin Institute*, 138, 401.

while another substance to produce the same apparent color absorbs a small percentage of the light from a broad band in the spectrum. In the first case as the solution is increased in depth or concentration, its color at first rapidly increases until all or nearly all of the rays of light which it is capable of absorbing are exhausted, and further increase in depth effects but little further change in color. In the second case, owing to the smaller percentage absorption of the light rays the color increases to a much higher limit, and in great depths the solution has a much deeper color than is possible in the former case where the action is confined to a narrow band in the spectrum.

A combination of absorption bands having different relative absorptions in the same solution gives rise to the change in hue so often noticed with changing depth or dilution. Thus it is a matter of common experience that a water which is a pure yellow or even greenish when seen in slight depth becomes orange and even quite red when seen in great depths. The way in which these differences occur was well shown by a diagram, in the report mentioned, showing how the standard matching the water at low depth, constantly diverges from it as the depth increases.

There are two possible means of remedying this evil. The first would be to secure a standard in which the coloring-matter was identical in composition with the coloring-matter in the natural waters. Such a standard could obviously be only the natural water standard, which, as shown above, is really no standard, but only a go-between between the waters and the real standards. The other method of avoiding the difficulty is to make comparisons only in such depths that the divergencies between the standards and the waters will not be considerable.

As stated in the report quoted above, the quantity of light transmitted decreases in geometrical progression as the depth increases in arithmetical progression. Let us say that the first cm. of water intercepts one per cent. of those rays of light, whose interception produces the effect of color in the water. The second cm. of water will then intercept one per cent. of the remaining rays, or 0.99 per cent., and the third cm. will intercept one per cent. of the 98.01 per cent. reaching it, or substan-

tially 0.98 per cent., leaving 97.03 per cent. As the color produced is measured by the difference between the light remaining and the full light, we may express the colors produced by one, two, and three cm. of water as, respectively, 1, 1.99, and 2.97. These figures are obviously substantially proportional to the depths; the error of one per cent. in the last case being entirely too small to be taken into consideration. If, however, the process is carried further, the error increases as rapidly as the square of the depth, and at no very remote point becomes important and serious. As an illustration of the substantial correctness of this proposition, the above-mentioned ortho- and paranitrophenols may be mentioned. Notwithstanding the most extraordinary differences between the colors of the comparatively concentrated solutions of these substances, the colors produced by extremely dilute solutions are substantially proportional to the amounts of the respective substances present, and so long as certain limits are not passed, their colors increase at the same rate with increasing depth. The differences between these substances at various dilutions are, however, vastly greater than those between the platinum-cobalt standard and natural waters, and the differences in the latter case with increasing amounts of color are no greater than would be sure to be found with almost any two coloring-matters not of the same chemical composition.

The point to which it is safe to carry the reading of colors is determined by practical experiment and not by theoretical considerations. It was stated by the author in the original paper that up to a point corresponding to colors of 0.9 in a depth of 200 mm. or corresponding lighter or deeper colors in greater or less depths, the variations between the hues of the platinum standard and actual waters were so slight as to be unimportant. In Mr. FitzGerald's report mentioned above, it is stated that colors up to a depth of 1.0 for the same depth can be satisfactorily compared with the platinum standard, this limit being ten per cent. above that suggested by the author, and as long as colors are not measured above these depths the errors introduced are entirely unimportant; and while it is recognized that serious errors might be introduced by the attempt to read much deeper colors, this contingency was distinctly provided against by stat-

ing that all waters with deeper colors should be read in a less depth of liquid, or what is practically more convenient, and as far as I have been able to ascertain, equally accurate, the water should be diluted with one, two or more times its volume of distilled water, the color of the diluted water read and multiplied by a proper factor. Mrs. Richards finds it necessary to adopt this same procedure, even with the natural water standards, because, as a matter of fact, the coloring-matters in different waters vary from each other, and the hues produced in different depths also vary in the same way as the hue of the platinum standard varies from that of a water, only in a less degree, and with the natural water standards it is only possible to read accurately colors as high as 2.0, or only twice as high as the limit with the platinum standard.

This dilution of waters with high colors may be objected to on the ground that, a water having, for example, a color of 2.0 does not in reality contain twice as much coloring-matter as a water with a color of 1.0, and that correct results will not be obtained in this way. This is, in fact, the case with the nesslerized ammonia standards and with the natural water standards based upon them, as was shown by the author, who stated that with these standards "color 0.5 is only twice as deep as color 0.2; color 0.8 is only twice as deep as color 0.3; color 1.0 is only twice as deep as color 0.4, etc.;"<sup>1</sup> and this very fact is one of the serious objections to the use of these standards. With the platinum standards, on the other hand, the numbers expressing the colors, as nearly as can be determined, are proportional at every point to the actual coloring-matters present, and this simple relation is one of the important practical advantages of the standard.

As a matter of fact, a great majority of the waters, even from swampy regions, have colors low enough to allow accurate direct readings with the platinum standard, and the necessity of diluting the more deeply colored waters occasionally found cannot be regarded as a practical objection to the process. In actual use the convenience of operation, the simplicity of the apparatus required, the accuracy of the work obtained even with unskilled

<sup>1</sup> American Chemical Journal, 14, 308.

operators, and the permanency of the standard, even under exceptionally unfavorable conditions, which has far exceeded anything for which we dared to hope when the standard was first used, have abundantly demonstrated its utility; and in view of the ease and accuracy with which it is possible to compare directly the colors of natural waters with metallic solutions, which are, in fact, the only reliable ultimate standards now in use or known, it seems most unfortunate and in every way undesirable to introduce arbitrary go-betweens, not having definite values of their own or capable of being reproduced or controlled except by comparison with other standards.

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### TECHNICAL ANALYSIS OF ASPHALTUM. No. 2.<sup>1</sup>

By LAURA A. LINTON.

Received January 3, 1896.

**M**Y former article<sup>2</sup> on this subject has been so favorably received and commented upon that I have been encouraged to offer a second contribution with the object of adding a few more facts to the literature of the subject, as well as to point out certain changes in the method of analysis outlined in the first article, which changes have been suggested by recent analytical work.

The method universally employed for the determination of the incorporated water of asphaltum is that of estimating the loss in weight of the substance when exposed to a temperature of 100° C. The possibility of a loss of more or less of the inherent volatile matter when heated to such a high temperature must have occurred to every one engaged in the analysis of asphaltum. A series of experiments made during the past few months has confirmed my suspicion that such is the case.

The experiment proper consisted in heating a weighed portion of asphaltum in a combustion tube, the general arrangement of the apparatus being the same as that employed in the determination of water in organic analysis. The temperature was gradually raised from the temperature of the room to that of boiling water. The tube was swept out before and after heating with either dried air or dried hydrogen. Simultaneously with

<sup>1</sup> Read at the Cleveland meeting, December 31, 1895.

<sup>2</sup> This Journal, 16, 809.

this experiment two other weighed portions of the same asphaltum were dried, one in an oven at  $100^{\circ}$  C. to serve as a check upon that portion dried in the combustion tube, while the other portion was dried in the sun.

As the method of sun drying requires several days it was done in a room as free as possible from dust and, to increase the temperature and at the same time to exclude all foreign matter, the samples were placed in large watch glasses with watch-glass covers fitting loosely to allow of circulation of air. In this lens-like arrangement the maximum temperature did not exceed  $50^{\circ}$  C. On cloudy days the drying was necessarily done in the oven below  $50^{\circ}$  C.

These experiments showed that the asphaltum tested did not oxidize below  $100^{\circ}$  C., as aspiration with dried air and dried hydrogen gave the same results; and also that all moisture is driven off below  $50^{\circ}$  C. while between  $50^{\circ}$  C. and  $100^{\circ}$  C., a certain portion of oily matter is lost, this oil invariably collecting in drops about the mouth of the combustion tube. In the light of these facts it becomes clear that the old method of determining moisture, if it is to be determined at all, is incorrect since the percentage lost on heating the asphaltum to  $100^{\circ}$  C. includes not only the water but also that part of the petroleum volatile below  $100^{\circ}$  C.

The moisture associated with an asphaltum being hygroscopic, as is evident from the fact that the same specimen carries a constantly varying proportion depending on atmospheric conditions, it should never be estimated as a constituent part of the asphaltum, particularly in making analyses for purposes of comparison.

In making all of my recent analyses, as a preliminary, I have air dried to a constant weight several grams of the sample to be analyzed before weighing out the portion to be treated with the different solvents, thus entirely excluding water from the percentage composition of the asphaltum.

A second departure from the method previously given is a purely mechanical one. As a matter of convenience I have discarded the use of the Erlenmeyer flask, the substance being weighed out on balanced filter-papers instead. In this way all digestion is done in separatory funnels. This method of treat-



ment is very simple and the results obtained are good, but care must be taken that the solution in the funnels does not become too concentrated before running off through the tap, otherwise the petroleum precipitates itself, more or less of it adhering to the outside of the filter-paper. To prevent this the petroleum ether may be drawn off every few minutes until the greater part of the petroleum has been extracted after which it is perfectly safe to allow the digestion to continue for hours in removing the final traces.

Lastly, I have obtained some interesting and, in my opinion, important results by fractionating the asphaltene, determining it in two portions: that soluble in boiling turpentine and that soluble only in chloroform. The process is a very tedious one on account of the difficulty of removing the very last trace soluble in boiling turpentine, but the results that follow are a sufficient warrant for the expenditure of so much time, which, for the specimens analyzed, ranged from one to four weeks. In order to secure concordant results in duplicate analyses I found it necessary to pursue the following course :

After the removal of the petroleum the residue on the filter was digested in boiling turpentine until the filtrate was colorless, when the contents of the filter were washed in alcohol and dried at 100° C. If, on drying, a black, semi-liquid substance separated from the mass, this was an indication that the turpentine fraction had not been entirely removed, in which case the process was repeated. In the most refractory specimens this treatment was applied many times. The tardy yielding to the solvent power of the turpentine is doubtless largely due to the fact that the turpentine does not readily penetrate the mass and it may be, also, that the chloroform fraction prevents the action of the turpentine just as gold protects silver from the action of nitric acid. The completion of the process is always indicated by the appearance of the dried residue which, after the complete removal of the turpentine fraction, is invariably a loose, brown powder without coherence. This treatment shows that part of the asphaltene soluble in boiling turpentine to be a black, viscous, semi-liquid substance resembling tar and having a melting point at or below 100° C.

Another fact, which may prove valuable as well as interesting, is clearly brought out in this fractionation of asphaltene and that is that not only do the "aged" varieties of asphaltum contain a larger percentage of asphaltene but the turpentine fraction becomes a smaller proportion of the total bitumen while the chloroform fraction becomes larger.

An investigation of the table of the percentage composition of the following varieties of asphaltum will confirm this statement:

No. 1. An average sample of land asphaltum from the island of Trinidad.

No. 2. Altered or "aged" (iron pitch) Trinidad land asphaltum.

No. 3. Altered or "aged" Trinidad land asphaltum.

No. 4. An average sample of Trinidad lake asphaltum.

No. 5. An altered or "aged" Trinidad lake asphaltum.

No. 6. An altered or "aged" Trinidad lake asphaltum.

No. 7. An altered or "aged" (iron pitch) Trinidad lake asphaltum.

No. 8. Asphaltum from Montague Co., Texas.

No. 9. Turrellite from Uvalde Co., Texas.

No. 10. Asphaltum from near Ardmore, Indian Ter.

No. 11. Grahamite from Ritchie Co., W. Va.

No. 12. Scyssel asphaltic rock from Eastern France.

Sam- ple.	Petroleu- ene.	Turpen- tine fraction.	Chloroform fraction.	Asphal- tene.	Total bitumen.	Ratio of chloroform to total bitumen.		Organic matter not bitumen.	Mineral matter.
						total	fraction to		
1	33.73	15.67	3.179	18.849	52.579	1 : 16	11.528	35.886	
2	33.574	13.7	9.627	23.327	56.901	1 : 6	8.414	34.684	
3	21.362	15.2	15.112	30.312	51.674	1 : 3	9.85	38.375	
4	35.40	12.300	5.287	17.587	52.987	1 : 10	10.962	36.100	
5	26.925	18.613	6.687	25.3	52.225	1 : 8	11.237	36.537	
6	19.25	22.35	10.962	33.312	52.562	1 : 5	9.562	37.875	
7	22.25	9.785	12.54	22.325	44.575	1 : 4	8.937	46.462	
8	7.538	1.601	trace	1.601	9.139	....	....	90.861	
9	8.786	3.267	trace	3.267	12.053	....	....	87.947	
10	9.503	0.9905	trace	0.9905	10.4935	....	....	89.5065	
11	49.959	17.458	32.583	50.041	100.00	1 : 3	....	....	
12	7.486	3.945	0.371	4.316	11.802	1 : 31	....	88.198	

I am not yet prepared to say that the turpentine fractionation of asphaltene, if made in the case of the asphaltum obtainable from

different parts of the world would indicate the relative "ageing" of the different varieties, but my experience with Trinidad Pitch inclines me to think that this will prove the case when such analyses are made. However, even if the turpentine determination should prove of no value as indicative of "ageing" processes in asphaltum, there is still a weighty reason why it should not be abandoned.

The marked physical difference between the turpentine and chloroform fractions would seem to indicate the probability of a chemical difference and I am sure that when an ultimate analysis of asphaltum has been made, as it will be in the near future, that turpentine as a solvent will be proven to have its place.

I am aware that some object to the use of turpentine because it is not pleasant to work with, particularly when it is boiling hot, but in scientific research we are seeking truth and not our own pleasure and convenience. If the cooperation of chemists engaged in the investigation of asphaltum could but be secured the solution of the problem would be a speedy one. But this may not be, so solvents are accepted or rejected at will with apparently no principle ruling in the choice. One chemist of wide reputation rejects chloroform and uses carbon disulphide as the final solvent in the extraction of bituminous matter.

I have analyzed many different varieties of American and foreign asphaltum and, with the exception of the Neufchatel, which is practically all petroleum, and the asphaltum from Texas and Indian Territory, all yielded more or less bituminous matter on treatment with chloroform after exhaustion with other solvents. Now, because the Neufchatel and a few other varieties need no chloroform for the extraction of bitumen, shall this solvent be stricken from our category? rather let our scheme be so broadened as to be applicable to every variety of asphaltum the earth holds.

UNIVERSITY OF MICHIGAN.

#### DISCUSSION.

*A. H. Sabin* : This asphaltum business is one of a great deal of commercial importance. There are a great many things about it that we do not know: I hope somebody here can tell us a few things.

In the first place asphalts are a very peculiar set of bodies. The most attention has been given of late years to Trinidad, because it has been used for paving purposes, and has been of immense commercial importance. It has generally been overlooked by the chemists who have worked on this line, that comparatively recently the commercial introduction of asphalts from other sources has been of great importance. Ordinarily chemists analyze either the Trinidad or Egyptian asphalts. The Egyptian asphalt is considered to be a representative of the high grade asphalts which are to be found in the East, while the Trinidad asphalt is a cheaper variety, very elastic, and contains a large amount of foreign matter. Commercially, as a matter of fact, the Egyptian asphalt is higher priced than the American, and so are all the Eastern asphalts. The fact has been known for a number of years that large deposits of asphalt are found in Utah and Colorado known as Gilsonite and Uintahite. These have been put on the market at such low prices that in St. Louis, I understand, Gilsonite is used in the paving trade. Gilsonite is an exceedingly pure asphalt. It is a very interesting substance, and it is to be hoped that future investigations will take into consideration the fact that these more recently discovered beds, which promise to be of more commercial importance than the Trinidad deposits, are practically inexhaustible. Some asphalt deposits are being developed in South America. We have the general statement made in Dana's Mineralogy, which so far as I can learn is based upon the well known investigations made long ago in France, and partly on some work chiefly in the line of checking results, which was done in the Sheffield Scientific School, that all petroleum contain more or less asphalt in solution, and that it is generally believed that asphalts are a sort of petroleum residue, and that the natural asphalts differ from the asphalts which are obtained as petroleum residues in being oxidized compounds. As near as I can find out that term "oxidized" is merely a conventional term. It means that the hydrogen has been removed, not that the oxygen has been added, although they show upon analysis that some oxygen is present. The chief difference apparently is that compounds containing hydrogen have escaped. The differ-

ence between hard and soft asphalts is just, that difference that the mineral oils have been removed in some way or other from the asphalts and they are therefore hard; whereas some of them like the Trinidad have a considerable amount of mineral oily matter in them and are very elastic and well adapted to paving purposes. The presence of these ingredients, while it adds to their durability, detracts from their usefulness for other technical purposes, because mineral oil is comparatively easily removed by the action of the weather, while the hard asphalts not containing this volatile and soluble matter can be made elastic by being compounded with linseed oil and other substances, and in that way can be made immensely more permanent than elastic asphalts. This is inapplicable to paving, but it has large application. There is a good deal of commercial asphalt on the market under the name of Maltha, which was used as long ago as the time of Pliny. The name has been applied recently to asphalt from southern California. It is obtained in various degrees of hardness from a thick liquid to a solid, and is a good illustration of the so-called artificial asphalts. Of course, it is a natural product. Nothing has been done to it except the volatile portions have been distilled out of it. I should like to know whether these asphaltic constituents are present in all petroleum, or whether they are in some cases or in all cases produced by the action of high temperature upon the crude oil, and whether these differ from natural asphalt in oxidation or in what way?

*Prof. Mabery:* I have had some experience with asphalts in the way of observation, and to a certain extent experimentally. At Oil Springs, in Canada, a surface oil is found that is very heavy, with a specific gravity of 90 and in the vicinity of beds of asphaltic pitch. There is no question that there has been a change through the heavy surface oil into the asphalt. Some constituents of petroleum are very unstable; for example, at a temperature of 80°, in vacuo, a distillate was collected, which, after standing two years and then again distilled, decomposed into tar which could not be distilled without carbonization, doubtless the result of polymerization.

In regard to the origin of petroleum there is a great deal of

conjecture. So far as oxidation is concerned, the amount of oxygen contained in it is small. Recently we examined a product made from petroleum residue which resembles in some respects natural asphalt. It may be that some of you have heard of it under the name of Byerlyte. It is manufactured in this city. The process consists in taking the heavy oil after the burning oil is distilled, putting it into the still, passing in currents of air and applying a gentle heat to the bottom of the still during five or six days. Then the product is drawn off. It contains no fixed carbon. It resembles in some respects natural Gilsonite. So far as practical uses are concerned they are closely related. With reference to oxidation the quantity of oxygen does not appear to be very different from that in crude oil. As Mr. Sabin suggests, we cannot look upon oxidation in the production of asphalt as the introduction of oxygen, but rather as the removal of hydrogen, and that is doubtless related to certain features of polymerization. It seems to be a conversion of the unstable hydrocarbons into higher products. Concerning the composition of these products we know very little.

Other products have come under my observation which are on the market at the present time and used for insulators.

In some heavier sludges polymerization takes place when substances are formed closely resembling asphalt. There is a great field of investigation surrounding asphalt, but it is an exceedingly difficult subject.

The determination of water is an interesting question. It is practically impossible to remove water from petroleum by the ordinary methods. Ohio and Canada petroleum may stand for months, and when it is again distilled, water will appear to a considerable extent. Those pure hydrocarbons, which I showed last evening, can not be dried with calcium chloride. We found the moisture could only be removed by sodium, and after it is removed, upon exposure to the air, it reabsorbs moisture with great rapidity. Probably the same thing would apply to asphalt. Of course, in heating, the water will be removed, but if the products are again exposed to the air they will reabsorb the water. This question should be undertaken from the standpoint of thorough chemical investigation.

*Mr. Sabin :* These artificial asphalts have some very remarkable commercial differences from the natural asphalts. For example, they resist the action of sodium hydroxide. Sodium hydroxide seems to combine with almost all natural asphalts, but not with pitches or tars. In the same way for the purpose for which I use it, it is impossible to use it as asphalt, or in the way in which you can use any natural asphalt. You can not melt it alone without decomposition. It can be melted with other substances, such as rosin or some mineral oils. But it does not mix with the vegetable oils, such as linseed by itself. It is used very successfully as an insulator, as many of the pitches are. It has many useful and valuable qualities, which none of the asphalts have, especially that of resisting caustic alkali, but for many purposes it differs as widely from natural asphalt as if it were entirely and absolutely a different substance.

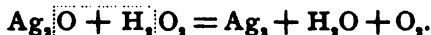
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## REVIEWS.

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### THE VALENCY OF OXYGEN AND THE STRUCTURE OF COMPOUNDS CONTAINING IT.

*Hydrogen Dioxide.*—In a recent issue of the *Berichte der deutschen chemischen Gesellschaft*<sup>1</sup> J. W. Brühl calls attention to the significance of recent work of Moritz Traube upon the structural formula of hydrogen peroxide. Traube found that when, in the electrolysis of water, the electrodes are separated by a diaphragm, no hydrogen peroxide forms. If now air be blown through the solution in contact with the cathode, hydrogen peroxide forms in quantity, presumably by the oxidation of the nascent hydrogen by the molecular oxygen of the air. Traube has also shown that when silver oxide is reduced to metal with formation of water and free oxygen, the latter comes from the peroxide, the oxygen of the water coming from the silver oxide, thus :



The constitutional symbol of hydrogen peroxide is usually written H.O.O.H. If this be correct we should expect it to unite with the olefines forming glycols by direct addition. Glycols seem not to be formed in this way, except in the case of

<sup>1</sup> 28, 2847.

ethylene glycol, which, according to Carius,<sup>1</sup> is formed by adding ethylene to hydrogen peroxide in "verhältnissmässig sehr Kleine Mengen." But even if this reaction takes place it would not prove the correctness of the above structural formula since glycols are formed by acting on the olefines with potassium permanganate. The formation of hydroxides by the action of hydrogen peroxide on the metals, such as zinc, is inconclusive for the same reason.

Neither does the formation of salts, such as barium dioxide from hydrogen peroxide prove anything, since we know many acids which contain no hydroxyl.

Because of the fact that in all its decompositions, molecular and not atomic oxygen, was liberated, and of its formation from molecular oxygen and atomic hydrogen, Traube wrote the symbol :



Additional interest attaches to this question since Wolfenstein has shown<sup>2</sup> that hydrogen peroxide may be concentrated and obtained by distillation in a vacuum as an explosive, nearly anhydrous substance.

Spring has recently shown<sup>3</sup> that thick layers of hydrogen peroxide have a bluer color than water, and since ammonium iodide is colorless, and  $\text{NH}_4\text{I}_2$  and  $\text{NH}_4\text{I}$  are green or violet, this indicates the possible presence also of molecular oxygen in the peroxide.

From his determination of its specific heat Spring concludes that the elements H, and O, in combining have used only a part of their potential energy, which is more nearly in harmony with Traube's formula than with that commonly accepted.

Brühl has now<sup>4</sup> determined the index of refraction of the pure nearly anhydrous substance and the specific gravity, and from these he has calculated the specific refraction and dispersion and the molecular refraction and dispersion. The molecular refraction and dispersion is found to be :

$$M_a = 5.791.$$

$$M_{Na} = 5.817.$$

$$M_\gamma - M_a = 0.136.$$

If we subtracted from the corresponding constants for water, the constants for the hydrogen atom, the values for the latter being nearly the same as in its compounds, we get the following :

<sup>1</sup> *Ann. Chem.* (Liebig), 126, 209.

<sup>2</sup> *Ber. d. chem. Ges.*, 27, 3307.

<sup>3</sup> *Ztschr. anorg. chem.*, 8, 424; 9, 205.

<sup>4</sup> *Loc. cit.*



	$M_a$ .	$M_{Na}$ .	$M_\gamma - M_a$ .
HOH .....	3.69	3.71	0.09
H.....	1.10	1.05	0.04
HO .....	2.59	2.66	0.05

This would give, doubling these values for hydrogen peroxide :

	$M_a$ .	$M_{Na}$ .	$M_\gamma - M_a$ .
H.O.O.H .....	5.18	5.32	0.10

These values are, however, much smaller than those observed for hydrogen peroxide, (see above). The easiest explanation of the fact that the spectrometer constants of hydrogen peroxide are considerably larger than would correspond to the symbol H.O.O.H, lies in the assumption of multiple union between the oxygen atoms. This would necessitate the assumption of multiple union in ordinary oxygen, and while this is not proven, it is indicated by the recent work of Olszewski and Witowski,<sup>1</sup> and especially by the work of Liveing and Dewar<sup>2</sup> on liquid oxygen. If we compare the optical equivalents of two atoms of oxygen in water with the constants of molecular oxygen, we get :

	$M_a$ .	$M_{Na}$ .	$M_a - M_\gamma$ .
2O in water .....	2.968	3.212	0.036
O <sub>2</sub> as molecular oxygen { liquid .....	3.958	3.964	0.069
{ gaseous ....	....	4.09	....

This shows that the optical constants of the molecular oxygen are considerably greater and the dispersion double that of the oxygen in water. This is, however, the best criterion of multiple union of the atoms.

But if in hydrogen peroxide the oxygen atoms are united by multiple union, fewer valencies must be concerned than in molecular union.

If this conjecture be granted, we should find the oxygen constants from hydrogen peroxide somewhat smaller than the molecular oxygen, and this is the case, as is seen below :

	$M_a$ .	$M_{Na}$ .	$M_\gamma - M_a$ .
Oxygen in water (2O).....	2.968	3.212	0.036
Oxygen, O <sub>2</sub> , in hydrogen peroxide..	3.591	3.717	0.055
Oxygen, O <sub>2</sub> , molecular { liquid ....	3.958	3.964	0.069
{ gaseous....	....	4.09	....

If we assume Traube's symbol for hydrogen peroxide to be correct, we must call oxygen trivalent, for which we have no

<sup>1</sup> Bulletin Acad. Cracovie, Oct. 1891, 341.

<sup>2</sup> Phil. Mag., 37, 268.

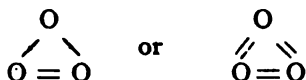
warrant; neither is any member of the oxygen group of the periodic system known with a valence of three.

On the contrary, sulphur, selenium and tellurium are bivalent and quadrivalent, and several compounds indicate the quadrivalence of oxygen, such as Rose's quadrantoxides,  $(Ag_2O)_4$ , but especially the compound of Friedel<sup>1</sup>  $HCl(CH_3)_4O$ . If it be granted that oxygen may be quadrivalent, we may then write hydrogen peroxide:



All the known properties of hydrogen peroxide; its formation from nascent hydrogen and molecular oxygen; its decomposition by nascent oxygen; its endothermic decomposition are explained by this structural formula.

*Constitution of Ozone.*—On the assumption of the quadrivalence of oxygen, the symbol of ozone may be either



No data are yet at hand sufficient to decide this question.

*Constitution of Carbon Monoxide.*—For many years carbon monoxide has remained as the single illustration of the bivalence of carbon. If we assume that oxygen is quadrivalent, however, this difficulty at once disappears. The spectrometric behavior of carbon monoxide favors this view. Brühl has shown<sup>2</sup> that carbon monoxide has the following molecular refraction:

	M <sub>ref.</sub>
Found .....	5.04
Calculated for C:O .....	4.79

This small difference is, however, many times greater than the possible experimental error.

The assumption of the structure C:O for carbon monoxide involves the assumption of unsaturated oxygen in numerous carbon compounds; at least in those containing an uneven number of carbon atoms; but we have also many sulphur and nitrogen compounds in which these atoms are bivalent and trivalent respectively.

*The Constitution of Water.*—In another paper Brühl considers<sup>3</sup> the result of this new view upon the constitution of water. It is known that in aqueous solutions of salts of strong acids and bases, the observed alteration of the freezing and boiling points is nearly double the normal amount deduced from van't Hoff's

<sup>1</sup> *Bull. soc. Chim.*, 24, 160, 241.

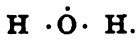
<sup>2</sup> *Ber. d. chem. Ges.*, 24, 663.

<sup>3</sup> *Ber. d. chem. Ges.*, 28, 2866.

equation. We know also that Arrhenius has accounted for this by supposing that in such solutions the salts are decomposed into their ions.

It is known, further, that many organic substances, such as the fatty acids, oximes, alcohols, etc., form double molecules or molecular complexes when dissolved in hydrocarbons, chloroform and carbon disulphide, and that these complexes are broken up when these substances are dissolved in water, and to a certain extent also when dissolved in alcohols, ethers, esters, ketones and phenols. The latter class of solvents are to a certain extent also ionizing, since when saturated with hydrochloric acid they act as conductors, while solutions of hydrochloric acid in benzene and other hydrocarbons are non-conductors.

Why water so far surpasses other solvents in its power to allow of this dissociation is not known, but the explanation is easily found if we write water as an unsaturated compound giving oxygen four bonds, thus :



In fact the properties of water indicate almost with certainty that it is unsaturated, for nearly all substances have a tendency to unite with it—are hygroscopic. Numerous hydrates and compounds with water of crystallization exist, and, finally, water is the universal solvent. The supplementary valencies of the quadrivalent oxygen are evidently the cause of the formation of the ions, and the molecular aggregates the reason of the dissociating power of the water.

This notion receives further support when we remember that all those organic solvents which are known as good dissociation media contain oxygen—ethers, alcohols, esters, ketones, phenols, urethane, etc.—while those free from oxygen, such as the hydrocarbons, chloroform, carbon disulphide, carbon tetrachloride have little or no power to cause dissociation.

EDWARD HART.

### THE HISTORY OF ELECTRIC HEATING APPLIED TO METALLURGY.<sup>1</sup>

Sir Humphry Davy is justly regarded as the father of dry electro-metallurgy. After making full allowance for the unusual facilities at his command, it still remains that his intelligent, faithful and extended use of his facilities is worthy of the utmost honor.

<sup>1</sup> Read before the Washington Section, Dec. 12, 1895.

It often happens, however, with epoch-making events that a close search reveals previous indications, so in this case it is found that not only was Davy's dry work preceded by a course of wet electro-chemical experiments, as pointed out by Davy himself, but also an important contribution to dry electro-metallurgy had been made long previous to Davy, and that this even preceded the first observed decomposition of water by the current.

In 1795 a Dutch book of 396 pages was published at Haarlem by Martinus Van Marum, entitled "Second Continuation of Experiments by Means of the Teyler Electric Machine."

I have not seen the original book, but various notices<sup>1</sup> of it appeared in the Journals of the time. From these it appears that Van Marum was a thoughtful and exhaustive investigator. His investigations took a wide range and included much outside our title. He, however, not only observed the heat produced by the passage of the current, but he actually measured it. In one instance the temperature of his apparatus, designed for measuring this effect, rose from 61° to 88° in three minutes, and to 112° in five minutes. He volatilized phosphorus in a tube and proved it to be "phosphor gas." He investigated the suitability of metals for lightning rods and determined that copper was twice as good as iron. He oxidized metals by the current and performed various melting experiments. He had a scale to measure the current and at twenty-four 100 feet of iron wire,  $\frac{1}{16}$  inch in diameter, melted, while 104 feet melted and separated into globules. He also melted longer pieces, but concluded that such melting tests were not worth the while. Sixty feet of No. 11 wire,  $\frac{1}{16}$  in diameter, melted at 24.5, but at the same point thirty-six feet of No. 1 wire glowed its full length, one-half being quite blue and the rest slightly oxidized. Quartz was split up and slightly melted.

Having oxidized the metals by the current, he conceived the idea that the oxides could be again reduced to the metallic state by the application of larger amounts of the current. It does not appear that he actually used electrically produced oxides to test this idea, for he not only did test it, but also actually collected and tested the gas given off.

His furnace, if I may so call it, was a glass tube with platinum electrodes. Into this he put his oxide and passed the current with the following results: Red lead gave lead on the surface of the tube in a few moments that could be gathered up, and in twenty minutes he collected three-quarters cubic inch of gas. White lead gave lead in smaller amounts. Tin oxide gave no metal.

<sup>1</sup> *Aellen J. der Physik.*, 4, 1; 6, 37, 360; *Neue J. der Physik.*, 3, 1; *Pog.*, 1, 68, et al.

Red oxide of iron gave no metal. Red oxide of mercury gave mercury and a little gas. He proved that the gas given off was oxygen and credits the decomposition to heat.

In a lecture delivered during the latter part of his life, Sir Humphry Davy gave a history of electro-chemistry, from which I take the following statements :

"The true origin of all that has been done in electro-chemical science was the accidental discovery of MM. Nicholson and Carlisle, of the decomposition of water by the pile of Volta, April 30th, 1800." "In the month of September, in the same year, I published my first paper on the subject of galvanic electricity in Nicholson's Journal, which was followed by six others, the last of which appeared in January, 1801. In these papers I showed that oxygen and hydrogen were evolved from separate portions of water, though vegetable and even animal substances intervened, and conceiving that all decomposition might be polar."

"In 1804, MM. Heisenger and Berzelius stated that neutro-saline solutions were decomposed by electricity, and the acid matter separated at the positive, and the alkaline matter at the negative poles; and they asserted, that in this way muriate of lime might be decomposed; and drew the conclusion that nascent hydrogen was not, as had been generally believed, the cause of the appearance of metals from metallic solutions."

"In 1805 various statements were made, both in Italy and England, respecting the generation of muriatic acid and fixed alkali from pure water. The fact was asserted by MM. Pachioni and Peele, and denied by Dr. Wollaston, M. Biot, and the Galvanic Society at Paris."

"It was in the beginning of 1806 that I attempted the solution of this question, and, after some months labor, I presented to the Society the dissertation to which I have referred in the beginning of this lecture. Finding that acid and alkaline substances, even when existing in the most solid combinations, or in the smallest proportions in the hardest bodies, were elicited by voltaic electricity, I established that they were the result of decomposition, and not of composition or generation; and, referring to my experiments of 1800, 1801, and 1802, and to a number of new facts, which showed that inflammable substances, and oxygen, alkalies, and acids, and oxidable and noble metals were in electrical relations of positive and negative, I drew the conclusions that the combinations and decompositions by electricity were referable to the law of electrical attractions and repulsions."

It is curious that Davy should have overlooked the very early work of Van Marum.

From this work Davy naturally passed to the question of decomposing the fixed alkalis by the current. It is not so much to the work itself, beautiful as it was, to which I wish to direct attention now, as it is to the fact that Davy not only did a vast amount of work and secured wonderful results, but he also clearly pointed out the principles involved, and at this early date enunciated the conditions of successful operation upon which the modern practical applications of electric heat to metallurgical operations rest.

He has so plainly traced the history of his work and pointed out the underlying principles that I cannot do better than quote his own words. He says :<sup>1</sup>

"In the first attempt that I made on the decomposition of the fixed alkalis, I acted upon aqueous solutions of potash and soda, saturated at common temperatures by the highest electrical power that I could command, . . . though there was a high intensity of action, the water of the solutions alone was affected, and hydrogen and oxygen disengaged with the production of much heat and violent effervescence.

"The presence of water appearing thus to prevent any decomposition, I used potash in igneous fusion.

"By this arrangement some brilliant phenomena were produced.

"I tried several experiments on the electrization of potash rendered fluid by heat, with the hopes of being able to collect the combustible matter, but without success, and I only attained my object, by employing electricity as the common agent for fusion and decomposition."

Here is the clearest kind of statement of the value of using the current for the double purpose of fusing the material to be acted upon, and for decomposing it. In modern practice this principle was used, notably in the Heroult process of smelting aluminum alloys, and is now used in the successful processes of extracting pure aluminum, such as the Hall process in the United States and its equivalents abroad.

Continuing, Davy said :

"The substance was likewise produced from potash fused by means of a lamp, in glass tubes confined by mercury and furnished with hermetically inserted platina wires by which the electrical action was transmitted."

This may be considered as a hint at electric heating under pressure, as proposed later by Werderman, de Groussilliers and Menges.

<sup>1</sup> Works of Sir Humphry Davy, 5, 58, 59, 60.

<sup>2</sup> Works of Sir Humphry Davy, 5, 61.

And in regard to the production of sodium he said :

"Soda, when acted upon in the same manner as potash, exhibited an analogous result ; but the decomposition demanded greater intensity of action in the batteries, or the alkali was required to be in much thinner and smaller pieces."

In modern practice the benefits to be derived from alloying the separated metals, at the moment of their reduction, with another metal, is an essential element of the Cowles and Heroult aluminum alloy processes, and also of various processes of the electrolytic production of caustic soda, notably Castner's process. Here too Sir Humphry Davy was early in the field with both work and word.

After describing various obstacles and the conditions necessary in decomposing the alkaline earths as an essential to success, he says :

"Or of combining them at the moment of their decomposition by electricity in metallic alloys, so as to obtain evidence of their nature and properties.

"Barytes, strontites and lime, slightly moistened, were electrified by iron wires under naphtha, by the same methods and with the same powers as those employed for the decomposition of the fixed alkalies.

"I had found in my researches upon potassium, that when a mixture of potash and the oxide of mercury, tin or lead was electrified in the Voltaic circuit, the decomposition was very rapid, and an amalgam or alloy of potassium was obtained ; the attraction between the potassium and the common metals apparently accelerating the separation of the oxygen.

"The idea that a similar kind of action might assist the decomposition of the alkaline earths, induced me to electrify mixtures of these bodies and the oxide of tin, of iron, of lead, of silver, and of mercury, and these operations were far more satisfactory than any of the others.

"These experiments were made previous to April, 1808.

"The earths were slightly moistened, and mixed with one-third of oxide of mercury, the mixture was placed on a plate of platina, a cavity was made in the upper part of it to receive a globule of mercury, of from fifty to sixty grains in weight, the whole was covered by a film of naphtha, and the plate was made positive and the mercury negative, by the proper communication with the battery of 500.

"The amalgams obtained in this way were distilled in tubes of plate glass, or in some cases tubes of common glass."

In modern practice the crucible or containing vessel is usually

<sup>1</sup> Works of Sir Humphry Davy, 5, 104, 107, 108, 111.

used as one of the electrodes, generally the negative. Sir Humphry Davy did the same, but like Siemens, made his crucible the positive pole, and in this particular case used external heat for fusing his charge. He says :<sup>1</sup>

"I fused a mixture of one part of silex and six of potash in a platina crucible, and preserved the mixture fluid, and in ignition over a fire of charcoal; the crucible was rendered positive from the battery of five hundred, and a rod of platina, rendered negative, was brought in contact with the alkaline menstruum.

"I tried similar experiments with mixtures of soda and alumina, and soda and zircon, and used iron as the negatively electrified metal."

The work of Sir Humphry Davy was followed by the work of Children, 1809-1815. In his first communication<sup>2</sup> he dealt mainly with the difference in the results produced by a battery consisting of a small number of large plates, and one consisting of a large number of small plates. The most interesting part of this paper, in tracing the history of metallurgical electric heating, is experiment 6, which is undoubtedly the first description of the passage of an electric current through a mixture of ore and resistance material, although it yielded no results. This principle was afterwards very successfully employed by the Messrs. Cowles. In this experiment of Children a mixture of sulphate of barium, red oxide of mercury and clay was submitted to the action of the current.

In his second paper<sup>3</sup> he described his work upon the relative conductivity of wires of various metals, and found that elevation of temperature affected the result.

He subjected various oxides, mostly of the rarer metals, to the action of the current, with varying results, some simply fused more or less, some were also reduced to metal. He also tried some experiments in simple melting.

His crucible consisted of a bit of boxwood charcoal, hollowed out on top with a little mercury in the cavity, serving as one electrode; upon this was placed a piece of the oxide; the other charcoal electrode was then brought near.

In this paper is also described Pepys celebrated experiment to determine that the diamond was really carbon. For this purpose a soft iron wire was bent and split by a saw; into the split some diamond powder was placed and bound in by fine wire, and the whole covered by leaves of talc. The current was then passed through the wire. The heat produced was not high, but the iron was carburized.

<sup>1</sup> Works of Sir Humphry Davy, 5, 119-120.

<sup>2</sup> Phil. Trans., 1809, 32.

<sup>3</sup> *Ibid.*, 1815, 363.



From this time on for over thirty years nothing seems to have been done in electric heating, although there were a few applications of the current to metallurgical processes in connection with external or other heat, such as the English Patents No. 9,946 of 1843, to A. Wall, for the use of the current in the blast furnace, and No. 10,362 of 1844, and No. 10,684 of 1845, to Napier for treating copper ore by the current in crucibles.

In 1848 and 1849 Despretz<sup>1</sup> published a series of articles in which he described the effect of combining the heat from three different sources, the electric current, the blowpipe and a burning glass. He clearly illustrates the difference between temperature and quantity of heat, the great difference there may be in the temperature of the source of heat and the temperature attained by the material heated, and that the loss of heat from the material heated may be supplied by a source of heat at a comparatively lower temperature and allow a higher temperature source of heat to exert its full heating effect. Thus on heating magnesia by the current at his command it simply became pasty, but on adding to this the heat of the burning glass it immediately volatilized in white fumes.

He determined that it is easier to volatilize carbon than to melt it; also that lime, magnesia and oxide of zinc behave in the same way. He melted alumina to a transparent glass; he also melted titanitic acid in various forms, oxide of iron and disphen.

He suggested the use of the current for melting metals practically, and melted eighty grams of palladium and 250 grams of platinum.

In his last communication Despretz described an arrangement in which a quantity current was passed through his crucible while a separate series current was passed through the contents.

In 1849 an English patent No. 12,772 was granted to Staite & Petrie, in which the current was applied to the treatment and fusion of iridium.

In 1853 an English patent No. 5 was granted to Watson & Prosser for the use of the current in converting iron into steel by which the time of conversion was to be shortened, and the quality of the steel improved. In one case the current was passed through the enclosing trough, and in another the poles were put into the cementing material surrounding the bars. These propositions seem to resemble some of the modern ideas of producing heat, but it is not clear that Watson & Prosser used sufficient current to produce any considerable heating effect.

Although I have not yet been able to locate the exact date, I mention here the Grove furnace which has been called the pro-

<sup>1</sup> *Compt. Rend.*, 28, 755; 29, 48, 545, 709; 30, 369.

tototype of the incandescent furnace. It consisted of a carbon crucible set in mercury, making the current connection, while the cover served as the other electrode. It was mentioned in *La Lumiere Electrique*, 19, 350, and *Scientific American Sup.*, April 24, 1886.

We come now to the first real attempt to employ the electric current to heat and act upon a charge of ore in a practical way. It is found in the invention of M. Pichon, patented in France, March 16, 1853, covered by English patent<sup>1</sup> No. 700 of 1853. In this process iron or other ores are mixed with carbon and shaken down between two or more pairs of electrodes through which the current is passing, when it melts, and after which it drops into an externally heated receptacle below.

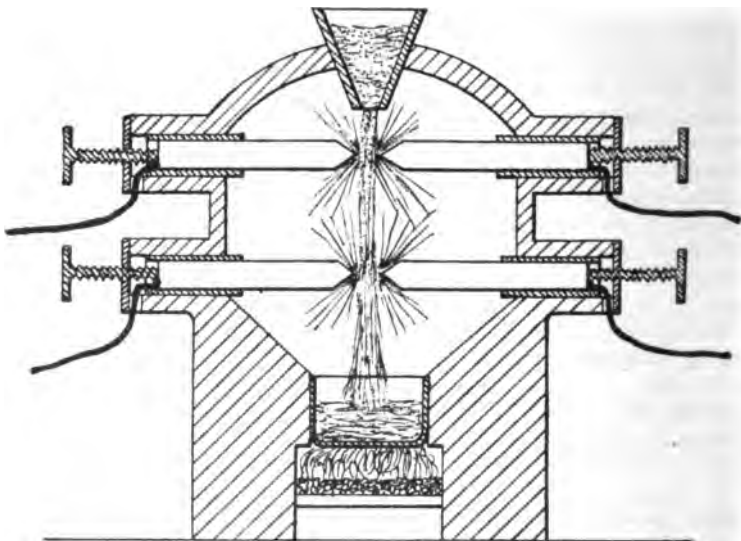


Fig. 1. Pichon's Furnace.

The description of this furnace (Fig. 1.) in *Practical Mechanics Journal* speaks of the electrodes as being very large, but I think that feet should be read inches.

In 1854 Duvivier<sup>2</sup> placed a piece of disthen in the electric flame and produced globules of metal.

There is another long break after 1854 in our subject, strictly speaking, although there were many metallurgical propositions in which the current was employed, but they were either wet processes, or else flame heat was employed.

<sup>1</sup> See also *Practical Mechanics J.*, 6, 257, and *Dingler*, 131, 415.

<sup>2</sup> *Compt. Rend.*, 38, 1066.

In 1866 Le Roux<sup>1</sup> published an exceedingly interesting and suggestive, but all too brief, communication upon the action of the arc upon lime and strontia. He decomposed lime and strontia in the arc and studied the reactions spectroscopically. He determined that the metals calcium and strontium were reduced, and carefully distinguished between the spectrum of the metals themselves and the spectrum of the white light resulting from the incandescence of the oxides. He asks the questions: Is the separation of the metals the result of electro-chemical decomposition? Is it due to vapor of carbon? Is it due to dissociation from heat alone? But he does not answer them.

We have seen that up to this time considerable work of a scientific character had been done from time to time in the field of dry electro-metallurgy, and that some suggestions at least had been made for the practical application of the current in this field. Undoubtedly, however, the cost of the current at this time was prohibitive. In looking over the field we can see the germs of modern processes, and easily imagine that if the early workers had been supplied with cheap current they would have carried their work very much farther, and developed practical electric metallurgical processes of value, but it remains as a fact that they did not have cheap current, and did not invent modern electric metallurgy.

With the development of the dynamo in the seventies came a wave of activity in the application of the current to metallurgy in the late seventies, and early eighties.

Before considering this growth in detail it is well to look at the advantages to be derived from the current as a heating agent. In doing this a sharp distinction between quantity of heat and degree of temperature should always be kept in mind. Unfortunately these terms are often used, even by persons who really know better, and who thereby mislead those who do not know better, as if they were synonymous. This is not at all the case. We may have an enormous quantity of heat developed at a low degree of temperature of which the pile of rotting apples is the old and familiar example. On the other hand, we may have a very high temperature developed by a small quantity of heat. A good blowpipe can melt fine platinum wire in a small blow-pipe flame. While the combustion of a given quantity of fuel will always supply the same quantity of heat the temperature developed may vary enormously. When we carry this consideration farther and apply it to the practical application of heat, this difference becomes much more marked and pronounced. For instance, a mixture of iron ore and carbon may be supplied with any quantity of heat at a low temperature without reduc-

<sup>1</sup> *Compt. Rend.*, 30, 1150.

ing the metal; or a mixture of bar iron and carbon may be heated indefinitely to a low temperature without producing steel, but once the proper degree of temperature is reached the required reactions take place. On the other hand, the proper temperature once attained, a sufficient quantity of heat at the right temperature must be supplied to carry on operations. While the good blowpiper can readily melt a fine platinum wire in his flame yet he cannot even soften a stout laboratory rod of platinum.

In practical work we are farther limited by materials of construction, their fusibility, their heat conduction and radiation.

The temperature attainable by ordinary combustion is limited by the temperature of dissociation of carbon and oxygen, which has been put at  $2500^{\circ}$  to  $2600^{\circ}$  C., but at such temperatures combustion is slow and losses of heat large, so that the practically attainable flame furnace temperature is probably about  $1800^{\circ}$  to  $2000^{\circ}$  C., while the practical oxyhydrogen blowpipe temperature may be several hundred degrees higher, but where the flame must not come in contact with the materials under treatment, and the heat must pass through the walls of a crucible or muffle, we must be content with a very much lower temperature.

With the electric current the conditions are changed. The first and most striking factor is the enormous temperature that can be both experimentally and practically reached. What the maximum temperature attainable may be has not yet been established, but temperatures about  $3800^{\circ}$  C. have been measured by Moissan and Violle. The second factor is that the heat can be developed right at the point where it is utilized, and the losses reduced to the minimum. This is especially advantageous in replacing muffle and crucible heating, as is also the fact that the heat is secured without the introduction of enormous quantities of products of combustion. Again, the temperature is under most perfect control, and can be adjusted with the utmost nicety. There are also minor advantages in the cleanliness and compactness of the operations.

It remains, however, that the cost of the current limits its practical application even now to a few special cases, and this is likely to remain so until the dream of the electrician of converting coal directly into current be realized.

In 1875 an English patent, No. 4,043, was issued to G. L. Fox for heating a crucible by the heat generated by resistance to the passage of the current, but curiously enough his resistance material was placed outside his crucible, and the heat had still to pass through the walls of the crucible.

In 1878 a voluminous French patent, No. 122,227, was issued

to M. Repieff, in which arrangements of electrodes for electric furnaces are shown. In the electric light part of his patent he also uses oxides to color his light.

In 1878 an English patent, No. 4,650, was issued to Clarke and Smith for producing ammonia by passing a mixture of nitrogen and hydrogen through sufficiently prolonged white heat produced by the electric arc.

The next electric furnace was that described in the celebrated English patent, No. 2,110, of May 27th, 1879, to C.W. Siemens. This may be said to inaugurate the era of electric furnaces proper, and to be the first real, hearty, and systematic attempt to make practical use of heating by the current.

As described in the patent with all its attendants of water cooled electrodes and regulating devices it is a formidable and elaborate piece of apparatus, but divested of its accessories its real operating parts become simply a crucible provided with two electrodes, arranged either vertically (Fig. 2) or horizontally (Fig. 3), through which the current passes.

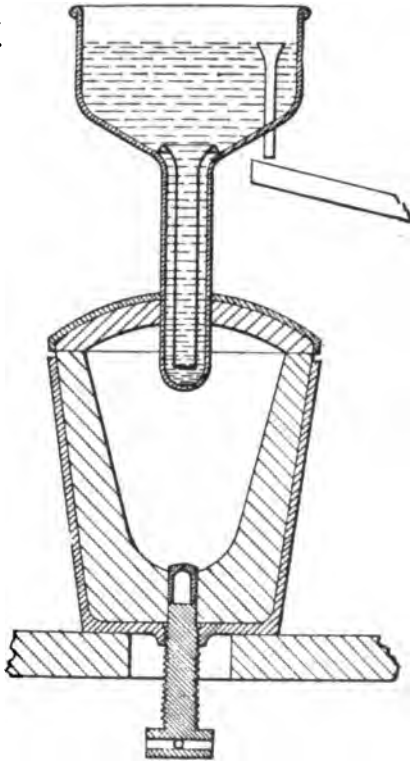


Fig. 2. Siemens' Furnace.

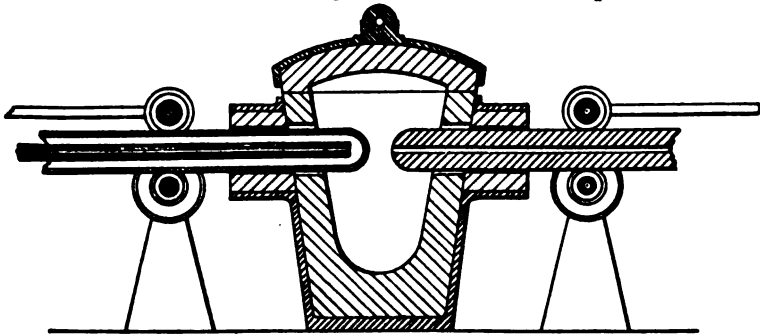


Fig. 3. Siemens' Furnace.

This apparatus was described and exhibited in actual operation before the Society of Telegraph Engineers' and the British Association<sup>1</sup>. The descriptions and exhibitions were confined for the most part to simple melting operations, although some attempts to saturate iron with carbon are described. It does not appear that Siemens ever used his furnace for the reduction of metals, although the article in *Iron* suggests that it might be so used. The death of Siemens undoubtedly cut off work in that direction with this apparatus.

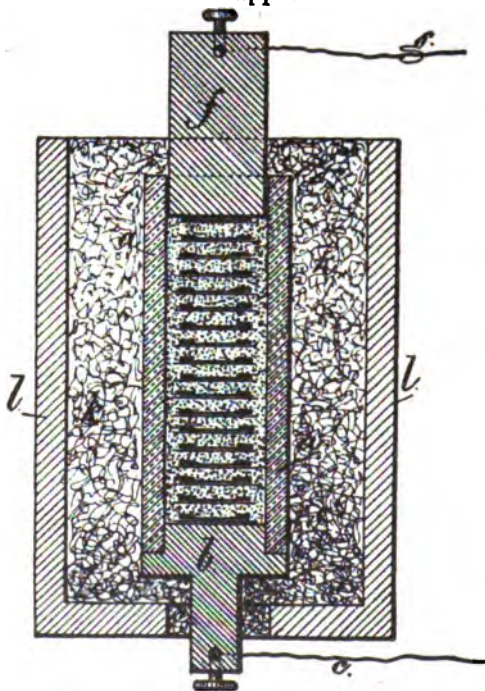


Fig. 4. Ball and Guest's Furnace.

In 1881 a United States patent, No. 236,478, was issued to Ball and Guest for an electrical carbonizing apparatus (Fig. 4) to produce carbons for the electric light. The articles to be carbonized are placed in a pile within a case and are surrounded by pulverized carbon. The case is then brought into the circuit and the contents thereby heated. A portion of the current passes through the carbon packing.

In 1881 an English patent, No. 304, was issued to Werderman for preparing carbon from sugar, which was then subjected in a mold to a white heat by the passage of the current,

for use in electric lamps. In the same year silicon was to be heated by the current to prepare it for use in electric lamps, French patent, No. 144,317.

The Belgian patent, No. 144,387, of Aug. 13, 1881, described a special form of furnace with one or more pairs of electrodes to be forced forward by springs. The furnace was calcined magnesia mixed with metallic oxides.

In the English patent, No. 3,757, of 1882, Werderman pro-

<sup>1</sup> *J. Soc. Tel. Eng.*, 9, 285.

<sup>2</sup> *Chem. News*, 46, 163; see also *Iron Supplement*, 1880, p. 424.

posed to heat silicon under pressure by the passage of the current.

At the Washington meeting of the American Institute of Mining Engineers, in February, 1882, in discussing the paper of Mr. Keith on the application of electricity to mining and

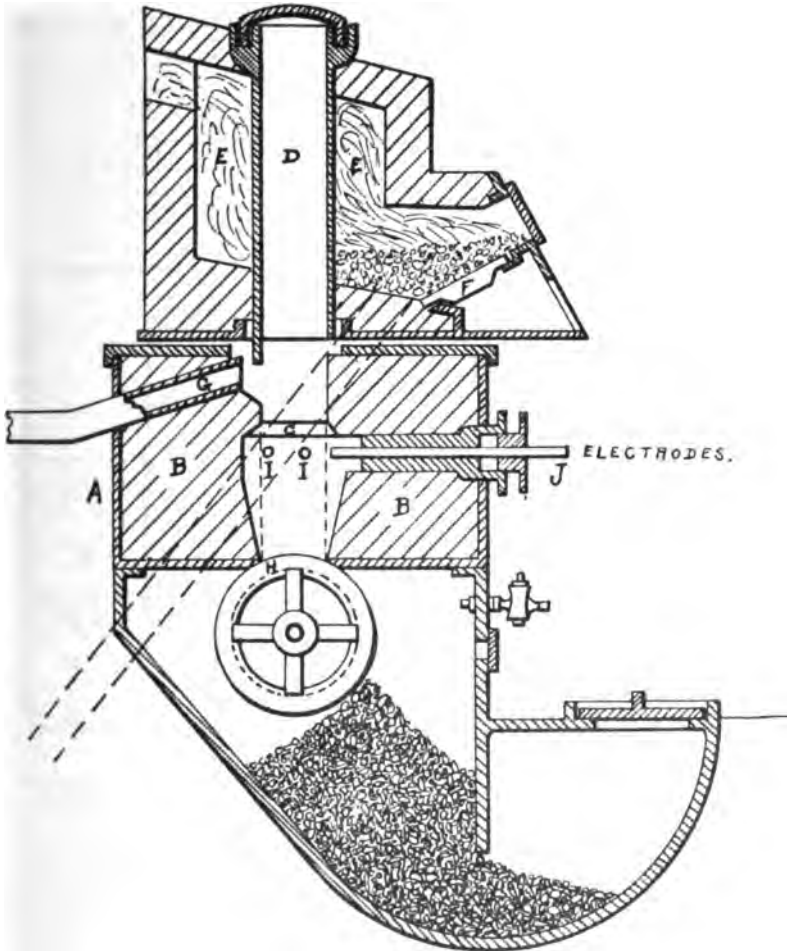


Fig. 5. Faure's Furnace.

metallurgy, Mr. H. M. Howe<sup>1</sup> briefly outlined a process which should have been developed into a successful commercial process. He said:

<sup>1</sup> Trans. Am. Inst. Min. Eng., 10, 317.

"The aluminous compound is placed in a carbon crucible, which is connected as the cathode of an electric current of great intensity. A voltaic arc is then thrown across from another electrode against this carbon crucible, the current thus first melting and then decomposing the aluminous compound, and metallic aluminum being deposited on the sides of the crucible."

In 1880-82-83-84 a series of patents<sup>1</sup> was issued to M. C. A. Faure, which has attracted considerable attention; more perhaps from their suggestiveness than from their actual contents. As described in the English patent, No. 6,058, of 1882, the process was designed for the reduction of sodium, and the furnace (Fig. 5) consisted of a tube in which the charge was first heated by an external fire. It was then passed into a chamber provided with electrodes for the passage of the current where it

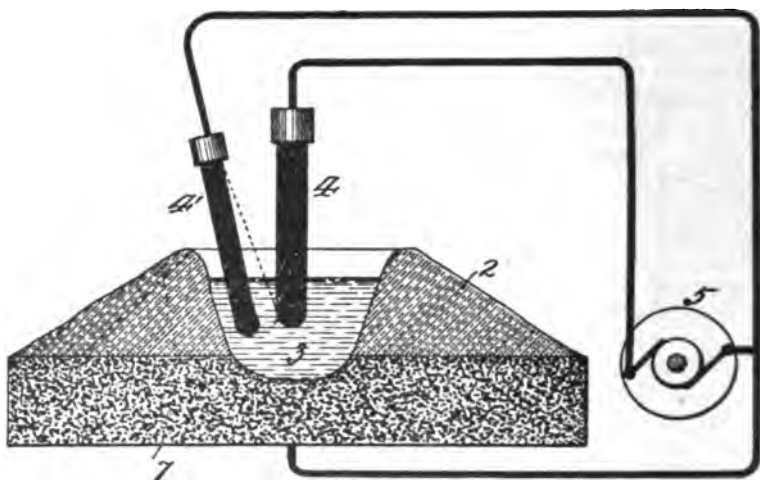


Fig. 6. Bradley's Furnace.

was intensely heated. Below was an automatic discharge for the refuse. There were also suitable condensing arrangements.

Chronologically considered, the United States patents to C. S. Bradley may be considered here, since the fundamental application was filed in February, 1883, although the patents were not issued for about nine years.<sup>2</sup> In these three patents (Fig. 6) the claims are drawn to cover three points. Using an unfused portion of the charge itself to enclose and contain the bath of fused material. Using the current for the double purpose of

<sup>1</sup> French patent No. 139,183. English patent No. 6,058, of 1882, and 5,489, of 1883, and Belgian patent No. 63,375.

<sup>2</sup> United States patents, No. 464,933, of Dec. 8, 1891; No. 468,141, of Feb. 2, 1892, and No. 473,366, of 1892.



fusing and decomposing the charge. Using a downwardly projecting blowpipe, or other flame, to supply a portion of the heat.

A United States patent, No. 282,964 was issued to Delaplaine, Hendrickson, and Clamer, in 1883, for melting the tin off from tin scrap by the current.

When, in 1885-86, the simple and beautiful process of Messrs. E. H. and A. H. Cowles' was announced, both the scientific and practical worlds were surprised and intensely interested, and a revolution in high heat metallurgy seemed imminent, particularly in the metallurgy of aluminum, but later developments have not fulfilled the early promises in general metallurgy, and aluminum metallurgy has now passed out of the field of high heats.

This process consists in mixing the ore to be reduced with a so-called resistance material (which for practical reasons was carbon) and then passing the current through. The current generated a very high heat and difficultly reducible oxides were reduced to metal. In the case of aluminum the reaction went a step farther, and the reduced metal combined with the carbon and formed a carbide of aluminum.

The generation of the heat was attributed to the passage of the current through the resistance material. This was not altogether so, but the high heat was generated by the passage of the current from particles of the charge to other particles, in other words, by dividing up the current into innumerable small arcs, and the great advantage of the process lies in evenly distributing the heat of a large arc through a considerable space, through which the material to be acted upon is distributed.

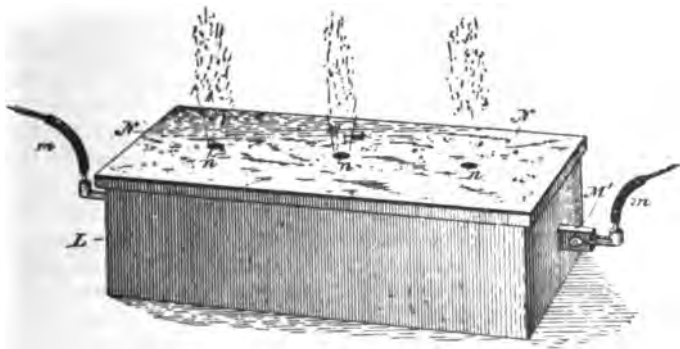


Fig. 7. Cowles' Furnace. (Outside.)

The furnace (Fig. 7) consisted of an outside case of brick

<sup>1</sup> United States patents Nos. 319,795; 319,945; 324,658, and others. Also foreign patents. The Cowles process was widely described. *Proc. A. A. A. S.*, 24, 136; *Trans. A. I. M. E.*, 14, 492; *J. Franklin Inst.*, 121, 111, and 122, 51 and 273; *J. Soc. Chem. Ind.*, 5, 206; *Mont. Sci.*, 1885, p. 1288, and 1886, p. 1032, *Industries*, Vol. 8, p. 273, 294, and elsewhere.

work, lined on the inside with carbon, then the charge containing the ore and carbon was put into the centre in contact with the electrodes, the charge was covered with carbon and a perforated cover placed over all.

By this process silicon, potassium, sodium, magnesium, calcium, chromium, and titanium, as well as aluminum were produced, but on account of so much of the aluminum combining with carbon it became necessary to introduce an alloying metal

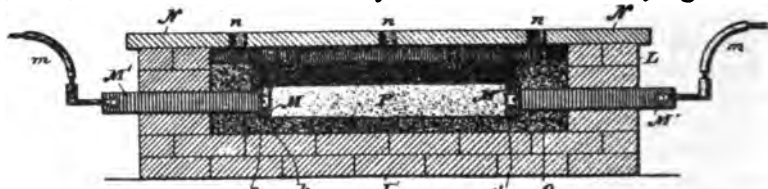


Fig. 7. Cowles' Furnace. (Inside.)

into the charge. This was usually copper or iron. By this process the price of aluminum in alloys was very largely reduced, but no considerable amount of the pure metal was ever produced.

In 1886 a United States patent, No. 335,499 was issued to Bradley and Crocker, in which the current was used to heat the charge, and was divided into two portions, one part passed through the walls of the retort, and another passed through the charge.

In 1887-88 a series of patents<sup>1</sup> was granted to M. P. L. T. Heroult, in which alumina was melted by the passage of the current and then electrolyzed with molten copper, or iron, as the cathode with which the separated aluminum alloyed.

The furnace (Fig. 8) was a suitable containing vessel of carbon to which the negative wire was attached. The positive electrode was of carbon. In running the furnace copper or iron was first put in and melted by the current, then alumina was added, which was also melted, and then electrolyzed by the current. More alumina and copper, or iron, were added from time to time, and the resulting alloy was tapped out periodically.

This was a very promising high heat alloying process, but it, as well as the Cowles process, was superseded in the aluminum field by the Hall process of producing the pure metal, of which it is only necessary to say here that in this process the charge is both melted and electrolyzed by the current, but the fact is to be emphasized that only a comparatively low temperature is required.

<sup>1</sup> French patent No. 170,003. Belgian patent No. 77,100. English patent No. 7,426, of 1887. United States patent No. 387,876. See also Richards *Aluminium*, 2nd ed., p. 36 and 309. *Trans. A. I. M. E.*, 18, 666. *Industries*, Vol. V, p. 405.

From 1892 to March 15, 1895,<sup>1</sup> there has been much published regarding the work of M. Henri Moissan, who has done so much fine work in the field of high temperatures, and has accomplished such wonderful results.

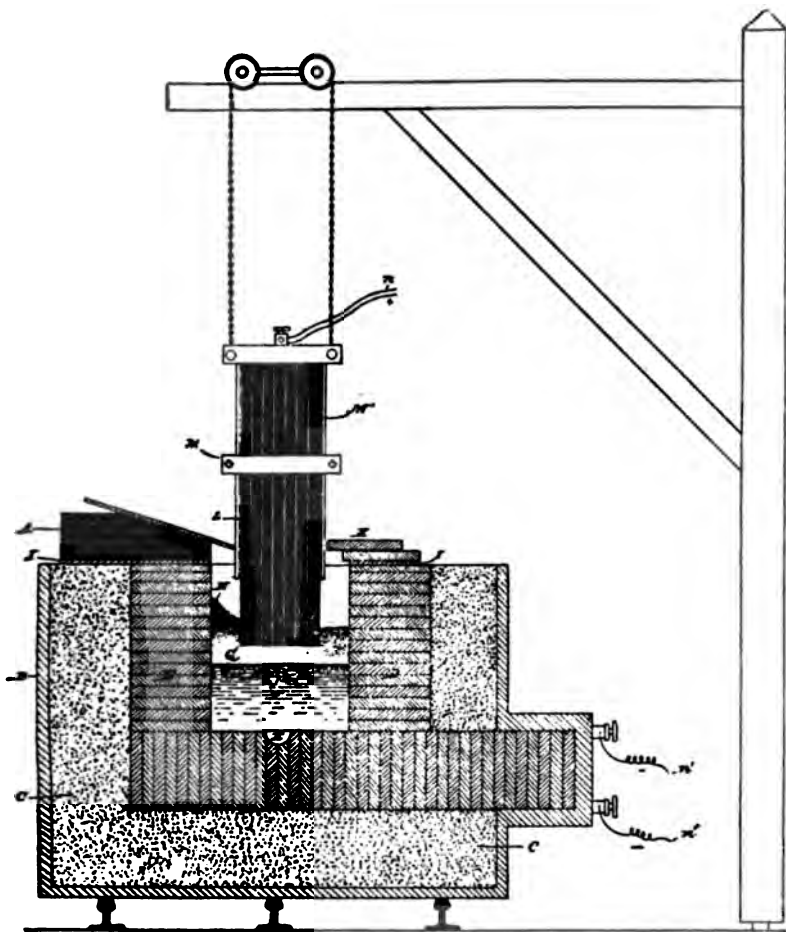


Fig. 8. Heroult's Furnace.

He employed various styles of furnaces and different amounts of current. His early furnace (Fig. 9) consisted of a simple block of quicklime suitably bound, and provided with electrodes

<sup>1</sup> *Compt. rend.*, 115, 1031; 116, 549; 117, 679; 118, 116 and 501. *La Nature*, Vol. 21, pt. 2, 1893, p. 225 and 275. *Ann. Chim. Phys.* [7], 4, 386.

and a cover. In this some very interesting results were obtained.

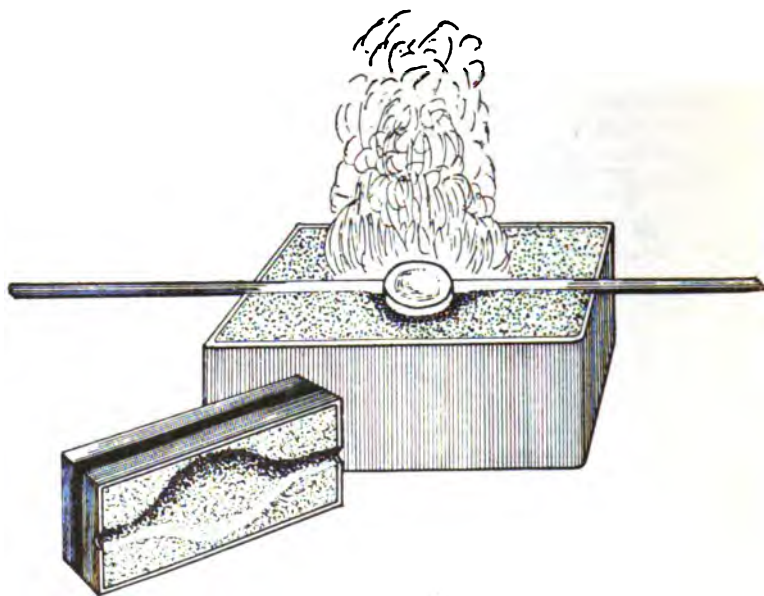


Fig. 9. Moissan's Early Furnace.

Another furnace (Fig. 10) was especially designed for determining the temperature by the specific heat method. A piece of carbon was

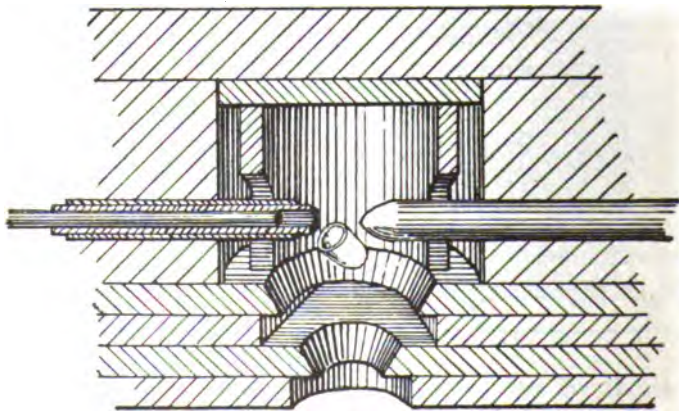


Fig. 10. Moissan's Specific Heat Furnace.

put on the end of one electrode, the current passed, and the carbon pushed off from the electrode, at the same time a slide was

withdrawn from the bottom of the furnace and the hot carbon allowed to fall in the calorimeter below. A number of temperature determinations were made in connection with M. Violle. Another furnace (Fig. 11) was provided with tubes for the intro-

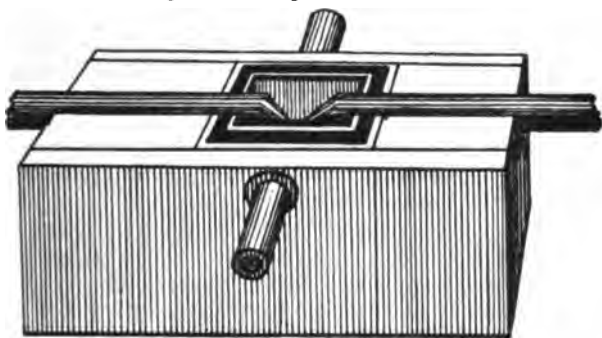


Fig. 11. Moissan's Furnace for Gas Reactions.

duction of gases. In this pure and colorless carbide of silicon was formed from carbon and silicon vapors. This furnace also had various layers, beginning with lime on the outside, and fol-

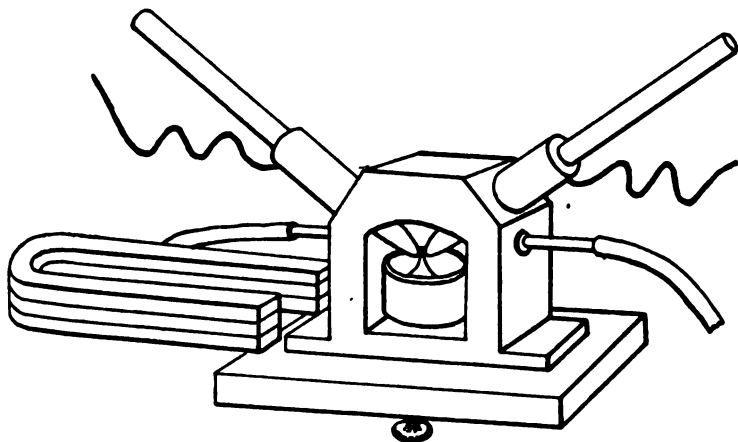


Fig. 12. Moissan's Furnace with Transparent Ends and Magnet.

lowed by carbon and then magnesia on the inside, or vice versa. Another furnace (Fig. 12) had transparent ends of glass, or mica, so that the operations could be watched. It also had magnets to direct and control the arc.

In this work Moissan designed to investigate and study the simple heating effect of the current separated as much as possi-

ble from any electrolytic effect. He speaks of and treats the arc as one would speak of an ordinary flame.

Moissan began with a very moderate current of thirty-five to forty amperes at fifty-five volts, and passed through various stages up to 1200-1600 amperes at 110 volts.

A few of the results obtained by Moissan may be mentioned. Magnesia was the only irreducible oxide found, it was melted and volatilized. Lime, strontia, and magnesia began to volatilize before melting. Lime was easily melted and the metal calcium reduced, but it immediately combined with the carbon vapor forming calcium carbide ( $\text{CaC}_2$ ). Alumina and platinum were volatilized. Artificial diamonds were produced. Various temperatures from 2000° to about 3800° C. were measured. Carbon begins to volatilize at about 3500° C. Various quantities of the rarer metals were reduced, 200 to 300 grams of uranium; 100 grams of vanadium; ten kilos of chromium, as well as manganese.

As in practical flame work the amount of fuel burned determines the temperature of the furnace, so in this case the amount of current passed determines the temperature and the furnace must be designed to stand the current to be employed. While Moissan's small furnace will stand the temperature developed by small currents, yet with 1200 amperes at 110 volts the lime and magnesia melt down, volatilize rapidly, and in a few moments the furnace is spoiled at a temperature of about 3500° C.

For materials of construction it was found that lime was the best nonconductor for heat, but its fusibility and the ease of forming the carbide, prevent its use for the inside of the furnace at very high temperatures. Compared with lime, carbon is a good conductor of heat. Magnesia is also a better heat conductor than lime. It does not form carbide of magnesium, and therefore can be heated very hot in direct contact with carbon, while lime cannot. It, however, is volatile, and can be melted at very high temperature. Practically, therefore, the outside of the furnace is quicklime, while the interior is variously lined with carbon or magnesia, or both, and when carbon is in direct contact with the lime it must not get too hot at the point of contact.

In 1893 a United States patent, No. 492,767,<sup>1</sup> was issued to E. G. Acheson in which a mixture of silica, carbon, and salt was heated by the passage of the current and silicon carbide produced, which has found considerable application as an abrasive.

In the present early stage and activity of the calcium car-

<sup>1</sup> See also *J. Franklin Inst.*, 136, 194 and 229; 137, 401. *Sci. Am.*, 70, 215. *West. Elec.* 17, 271. *N. Y. Sun*, Oct. 20, 1895. *Cassiers Mag.*, 9, 387.

bide and barium carbide questions it might not be wise to go into the details of the work and the claims of the various workers (Borscher, Maquenne, Moissan, Travers, Willson, I arrange these names simply alphabetically) but I mention these various carbide processes to show the present condition of our subject, and to draw especial attention to a notable fact.

In reviewing our subject we find that in the early days the current was suggested, tried and used for various metallurgical operations, in which both the heating and decomposing actions of the current were utilized. Then in the principal, practical part of the field, that of the production of sodium and aluminum, the generation of intense temperatures became paramount. This activity culminated in the high heat processes of Cowles and Heroult, and they were very soon superseded by the low temperature process of Hall for the production of aluminum, which carried with it the greater part of the demand for the production of sodium.

At the present day, therefore, there is no practical production of metals by high electric heats, with the possible exception of the production of chromium. On the other hand, high electric heats are being employed to go a step beyond the reduction of the metals, and to form new compounds, as in the carbide processes mentioned. In these the metals are first reduced, and are then immediately recombined with carbon, and thus in the field of high heat our subject becomes the application of high electric heat to chemistry.

Jan. 14, 1896.

FREDERIC P. DEWEY.

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#### NOTES.

*The Second International Congress of Applied Chemistry.*—The First International Congress of Applied Chemistry was held at Brussels, under the patronage of the Belgian Government, from August 4th to 11th, 1894. On the last day of the meeting it was voted to hold the next congress in Paris, in 1896. This approaching congress will be held in August of this year, the exact date to be hereafter published in this Journal, under the patronage of the French Government and pursuant to a plan of organization formulated by the Association of Chemists of the Sugar Industry and Distilling in France and the Colonies. M. Berthelot, the distinguished chemist, and now Minister of Foreign Affairs, is one of the Presidents of Honor. The congress will be held in ten sections, as follows :

Sec. I. Chemistry applied to the sugar industry.

Sec. II. Fermented and distilled beverages, cider, and vinegar.

Sec. III. Agricultural industries, including dairying, starch making, bread making, milling, etc.

Sec. IV. Agricultural chemistry, including fertilizers, soils, waters, cattle feeding, etc.

Sec. V. Chemistry applied to the customs, including methods of analysis of all the dutiable substances where the duty depends on chemical composition.

Sec. VI. Fats, tannin, rubber, paints, color, paper, etc.

Sec. VII. Photography.

Sec. VIII. Metallurgy.

Sec. IX. Biochemistry, foods, poisons, potable waters, microscopy, bacteriology, spectroscopy, etc.

Sec. X. Electrochemistry.

The undersigned committee for the United States has been appointed by the Provisional Council of the Congress, and we beg to call the attention of all American chemists, who expect to visit Europe during the coming summer, to the desirability of attending the meetings of the Congress. On application, the chairman of the committee will send a copy of the provisional program, showing the character of the questions which will be under discussion and containing a blank application for membership, which should be filled and sent to the proper address, before the date of the meeting. Already more than 900 chemists have entered their names as members of the Congress, and it is confidently expected that the membership will reach 2000. The committee respectfully invites the cooperation of all American chemists who hope to be able to attend the meetings or contribute papers for discussion.

Dr. H. W. Wiley, Dept. of Agriculture, Washington, D. C.,  
Chairman.

Prof. Peter T. Austen, Polytechnic Institute, Brooklyn, N. Y.

Prof. F. W. Clarke, U. S. Geological Survey, Washington,  
D. C.

Dr. Charles B. Dudley, Pres. Amer. Chem. Society, Altoona,  
Pa.



Prof. F. A. Gooch, Yale University, New Haven, Conn.

Prof. Charles Loring Jackson, Harvard Univ., Cambridge, Mass.

Dr. Wm. McMurtrie, 106 Wall St., N. Y. City.

Prof. Charles E. Munroe, Columbian Univ, Washington, D.C.

Prof. Albert B. Prescott, Univ. of Michigan, Ann Arbor, Mich.

Prof. W. B. Rising, Univ. of Cal., Berkeley, Cal.

Dr. G. L. Spencer, Centralia, Wis.

Dr. W. C. Stubbs, Audubon Park, New Orleans, La.

Dr. Thomas Taylor, Washington, D. C.

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*The Cyanide Method of Extracting Gold from its Ores. Application to the Assays of Ores Poor in Gold and Silver.*<sup>1</sup>—*Preliminary Notice.*—Having undertaken this work, at the suggestion of Prof. Mallet, only within the last two or three weeks, I have no exhaustive report of any nature to present. The work has not, as yet, advanced to such a stage that results can be stated satisfactorily in numbers. The attempts to apply this method to assay purposes *may* have been already made. If so, I have been unable to find any statement of that fact, and have no knowledge that such an attempt has been made.

I am at present comparing the method with the methods using chlorine and bromine. Quartz ores, too poor in gold or silver to be advantageously worked by the ordinary method of crucible assay, are the ores so far used.

The pulverized ore is well and repeatedly shaken with 0.25 per cent. solution of potassium cyanide, free access of air being provided for. After filtration and partial evaporation, the liquid is slowly passed over pure zinc filings. The zinc is then scorified with a larger amount of lead and the button cupelled.

The work has only progressed far enough to give hopes of good results. It seems at this stage to offer several advantages over the other methods mentioned.

The cyanide extracts the silver as well as the gold; bromine and chlorine only extracting the gold. The extremely disagreeable fumes of the other methods are entirely avoided. The work can be conducted without the use of hoods or fume rooms.

<sup>1</sup> Read at the Cleveland meeting, December 31, 1895.

The method yields the metals in a condition in which they can be more easily handled and their weights determined than can be the exceedingly fine precipitate from the bromine or chlorine solution.

The time is materially shortened, the long delay in the collection of the gold by the use of ferrous sulphate or oxalic acid being avoided.

In the few comparisons made, the amount of gold (and silver) extracted has been greater with the cyanide method than with the others. Though sufficient work has not as yet been done to make this reliable.

Before pronouncing on the availability of the method, other classes of ores than those so far used (quartz ore with and without pyrite) will be treated.

I expect to push the work as rapidly as possible.

*Jan. 3, 1896.*

WILLIAM J. MARTIN, JR.

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#### BOOKS RECEIVED.

Mining Journal of the Northwestern Mining Association. Spokane, Wash. 58 pp. Price 10 cents.

A Text-Book of Gas Manufacture for Students. By John Hornby, F.I.C. New York: Macmillan & Co., 1896. xiv, 216 pp. Price \$1.50.

Bulletin No. 59. Spraying Experiments in 1895. Lexington, Ky.: Kentucky Agricultural Experiment Station of the State College of Kentucky. December, 1895. 19 pp.

Bulletin No. 60. Analyses of Commercial Fertilizers. I. Official Analyses. II. Analyses of Farmers' and Inspectors' Samples. Lexington, Ky. Kentucky Agricultural Experiment Station of the State College of Kentucky. December, 1895. 12 pp.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### THE MANUFACTURE OF CALCIUM CARBIDE.<sup>1</sup>

BY J. T. MOREHEAD AND G. DE CHALMOT.

Received January 27, 1896.

**S**O universal is the interest in acetylene gas and so different the estimates and opinions as to the cost of calcium carbide as a source of the cheap production of acetylene gas, that we have thought it desirable to place on record the data from our actual experience in the production of calcium carbide in quantities. The works of the Willson Aluminum Company have been running night and day since May 1st, 1895, producing calcium carbide. These works are daily duplicating the results here given and can expand indefinitely. Each individual step, except water power, as taken at Spray, N. C., is capable of being changed in the direction of reducing the cost of the output, as these efforts have been attended with the clumsiness, lack of adaptability and excessive cost that is incident to all efforts along an untrodden path. Still we can produce calcium carbide at less than \$25.00 per ton, including wear and tear and interest on capital.

Beyond looking after the dynamos, no special training is necessary, as neither metallurgical nor chemical skill is required in the operations. We grind and mix coke and lime, start the water wheel, see that the arc is formed, shovel in the mixture of lime and coke and the volt- and ammeter show when to lower or

<sup>1</sup> Read Sept. 3d, before the Springfield meeting of the A. A. A. S. by one of us (M). We have made since then several additions, so as to make the article complete up to the present time.

raise the carbon pencils, which is done by means of a screw located in the dynamo room, away from the furnace. We can measure with an ordinary yard stick on this screw the height of the piece of carbide in the furnace. We stop when we have raised the carbon pencils thirty-three inches, switch the current off to another furnace and repeat the operation. The carbide in the former furnace, as soon as cooled and brought in contact with water, is all ready to do perfect work in generating acetylene gas; it will proceed with this work without help and will make room therefor in spite even of bands of steel.

Water power costs us \$6.00 per horse power. Water in the raceways ready for the water wheels is now offered in enormous quantities to the Willson Aluminum Company at the rate of \$5.00 per horse power per year. These powers are located at different places, where coke and lime can be had cheaply, and also cheap transportation for the carbide to the market.

The technical description of our process which follows herewith was written by G. de Chalmot, who has had for some time personal supervision of the operations of the Willson Aluminum Company.

In the year 1888 Mr. T. L. Willson started a series of experiments with a view of reducing refractory ores in the electric furnace, and among other valuable things he made calcium carbide.<sup>1</sup>

We will first give a short description of the furnace and a general outline of the process, then enlarge somewhat on the details. The furnace used in Spray, N. C., is built of ordinary brick (a sectional front view is given in figure 1). The front side is formed by four iron doors, the one above the other. The upper two remain closed usually. The chimney is attached near the top of the furnace, and commences with a flue in the corner. The furnace measures at the bottom inside two and one-half by three feet. The electric current enters at the bottom

<sup>1</sup> We will note here that Moissan, who discovered this process for making carbide, independently of Mr. Willson, communicated incidentally at the meeting of the French Academy of December 12th, 1892, (*Compt. Rend.*, 115, 1033) that a carbide of calcium is formed if calcium oxide is heated in an electric furnace with carbon electrodes. He investigated the compound much later (*Compt. Rend.*, 118, 50). Mr. Willson, who sent during the summer of 1892 samples of carbide for examination to Lord Kelvin, of the Glasgow University, clearly antedates Moissan. See Journal of Franklin Institute of 1895, page 333.—Note.

and top. The bottom electrode is an iron plate covered with eight inches of carbon b. For this covering we use pieces of

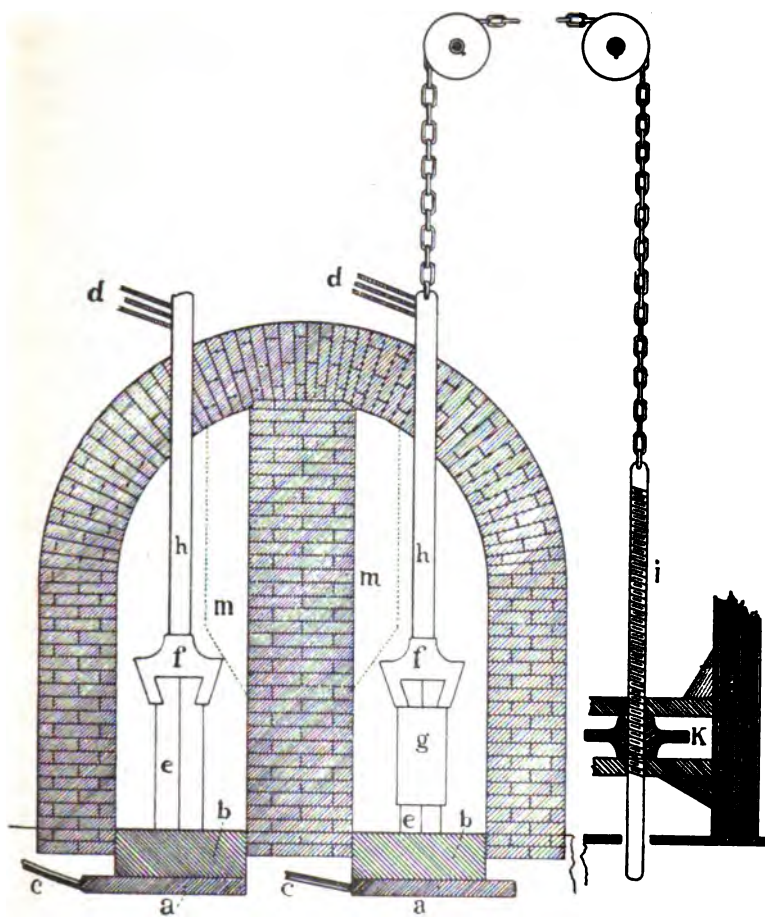


Fig. 1.

carbon pencils or a mixture of coke and coal tar. Sixteen copper cables of 0.75 inch in diameter c convey the electricity from the dynamos to the bottom electrode.

Sixteen other cables are connected with the top electrode d. The top electrode is composed of six carbon pencils e, each four inches square and thirty-six inches long. Six pencils are

arranged in three pairs behind each other and are cut out at the top so as to fit in the carbon holder f. They are enveloped together by a sheet of iron g, which is shown in the right handed furnace of figure 1. They really form one pencil. The carbon holder is screwed to a copper bar h, which is three inches square and to which the copper cables are connected. This bar is fastened by a chain that runs over two pulleys to a long upright screw i. On this screw is a nut which forms the center of a wheel k. By turning the wheel the screw can be raised or lowered. The man who attends to the wheel has the volt- and ammeter before him. The electric current is generated in two dynamos to which transformers are connected, and which can give a current of from fifty to 100 volts. The power is furnished by a water wheel of 300 horse power under twenty-eight feet fall.

Two of the furnaces have been working for twelve months and they have given satisfaction, except for working not sufficiently economically. In the furnaces built for the Niagara Falls Carbide plant, many changes which we suggested, have been adopted looking to economy of production. We give here a short description of these furnaces (figures 2 and 3).

In Spray it is necessary to allow the furnace to cool before emptying it. In order to use one and the same furnace continuously, the bottom of the furnace is replaced by an iron car a which runs on a track and in which carbide is formed. When the car is filled the pencils b have been lifted entirely out of it. The current is then shut off, door c is opened, the full car is run out and replaced by an empty car. The pencils are lowered again to the bottom of the car and a new run is commenced.

The bottom of the car is covered with from four to eight inches of carbon. When the contents of the car have sufficiently cooled outside the furnace, which will take from six to twelve hours, the body of the car is lifted from the track by the trunnions d and turned over. The contents are dropped on a grate formed of iron bars, on which the piece of carbide remains, while the unreduced material falls through into a lower room where it is collected to be used again for the formation of carbide. The mixture of lime and coke is fed into the car through the flues e,

which extend along the whole length of the car. The rods *f* which bear four blades, extend through the whole breadth of

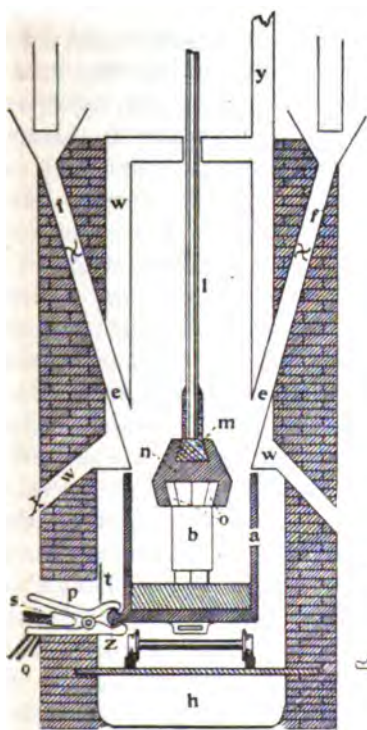


Fig. 2.

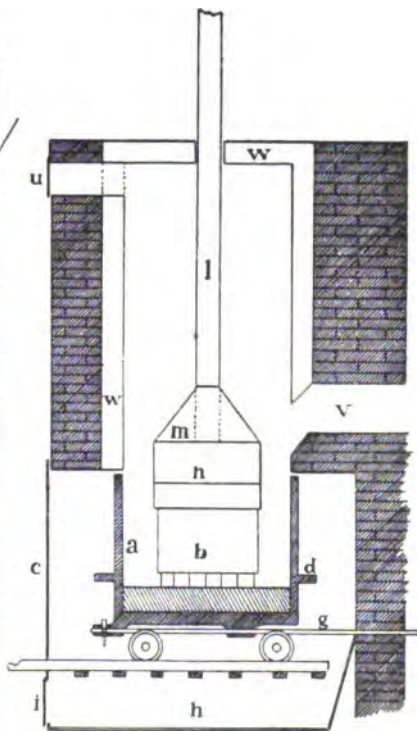


Fig. 3.

the feeding flues. These rods are turned automatically, and the faster they turn, the more material is fed into the car. In order to stoke the furnace automatically, the car is attached to an iron bar *g* by two hangers and a coupling in front of the car. Bar *g* extends through the back wall of the furnace, and is automatically moved forward and backward for about two inches and about twenty times per minute. The car is thus also rolled backward and forward on the track for about two inches each time. Every time that the car stops or starts it gets a little jerk which is sufficient to fill up the holes made by the escaping gases in the loose material. This motion of the car further prevents the arc being located for a longer time at one point, for

which the arc has always a great tendency. This will materially increase the efficient use of the heat of the arc. Under the track of the car is the bin h in which the unreduced material is collected that will fall from the car when this is taken out. This material can from time to time be taken out through the door i. The carbon holder is more complicated than in the Spray furnace. Twelve carbons are used and the holder is therefore about twice as heavy. It is not advisable to suspend this carbon holder from a copper bar, which moreover becomes rather hot in this closed furnace. The carbon holder is therefore attached to a rod l, which is composed of three slabs. The inner one is of copper and measures six by one and one-half inches, and the outer ones are of iron and are six inches by one. Since it is not practical to attach the twelve carbons in their iron casing to the carbon holder in the furnace, the holder itself is composed of two pieces, m and n, which slide into each other. The aggregate of pencils is connected to piece n outside the furnace and the whole is placed in the car a. Rod l is so far lowered that piece m will easily slide into piece n, and the connection can easily be effected. Iron plates o are placed between the carbon holder proper and the pencils. These plates o are about one inch thick. They are fastened to the inside of the carbon holder by pins which are inserted in the holder; and fit in holes of the plates. These plates can be easily removed and replaced. It will sometimes happen that a small arc is started between the pencils and the inside of the carbon holder and a part of the carbon holder will melt. In the case that the plates o are used, one can simply replace these plates. The car a forms one of the electrodes and is connected with the bottom cables q by two clamps p. The lower clamp is stationary and the upper one can be opened. The clamps are tightened around the appendage z of the car by a wedge and screw s. When the clamps are fastened the slide t is lowered so as to shut the opening. The electric connection with the car can also be and is better made through the bar g, which in that case is composed of an iron and a copper slab. It may also be made by two copper bars which run alongside of the car and are pressed against it with springs. The furnace is entirely closed.



When it is started the door c is shut, but the door u is kept open till the carbon monoxide, which is formed in the reaction, has replaced the air in the furnace. This point is reached when the flame comes out of this door. Door u is then also closed and the gases escape through the chimney v. The use of door u prevents explosions of the carbon monoxide in the closed furnace. Chimney v begins just over the car. The carbon holder and the rod l are therefore not in the current of the hot gases. The upper part of the furnace is cooled moreover by an air jacket w through which a draught of air is maintained. The cold air enters through openings x and the warm air is led off by chimney y. The warm air may be utilized for heating the building. The chimney gases pass through flues or rooms, in which the lime dust is collected by proper means. Owing to valuable suggestions of our superintendent, Mr. J. C. King, this furnace is called the King Furnace. Besides these two types of furnaces, several others have been proposed.

In order to start our present furnace, we shut the lower iron door and lower the pencils to the bottom of the furnace. The current is turned on and the mixture of coke and lime fed in, the arc being kept covered with the mixture as high as one foot around the pencils. It is then easier to keep the arc steady. It is necessary to stoke from time to time, for the gases which are formed in the arc constantly make channels through the material, and especially if unslacked lime is used. These channels will not fall in and less material will come into the arc. The feeding in of the material is continued for several hours. If the attendant at the hand wheel sees that the voltage becomes low, he raises the pencils. If the arc should be broken the amperage becomes zero and the voltage high, and in that case the pencils are quickly lowered. After shutting off the current it is well to allow the furnace to cool two or three hours before emptying it.

The carbide is always found in one piece between the pencils and the bottom. It has a conical form, being broader at the base and can be two and one-half feet high in our furnace. It however never has so great a diameter as to fill up the whole capacity of the furnace. The carbide is therefore entirely sur-

rounded by a cover of the mixture of lime and coke. This mixture is so bad a conductor of heat that the brick walls of the furnace are not attacked. It is very easy to separate the carbide from the loose mixture, for the latter never melts together, while the carbide is hard and solid. The pieces of carbide are covered with a thin coating which is a little thicker at the top of the piece, and the same may be reground and again used. This coating contains mainly carbon, but also carbide and calcium oxide. It seldom yields more than a half cubic foot of gas per pound, but in some cases it yields 1.77 and even 2.10 cubic feet. This coating, however, is of little importance. If the mixture is well made this coating seldom exceeds from twenty to thirty pounds on a piece of carbide of from 300 to 400 pounds. The carbide itself is crystalline. The crystals are especially well developed near the top and are more perfect with an excess of coke, low voltage and when allowed to cool slowly. The center of the piece of carbide stays liquid for some time after the electric current has been shut off. The liquid part, however, is of the same quality as the rest of the piece. We have in fact tapped out of the furnace, carbide which was very pure and yielded 5.59 cubic feet of gas per pound. We do not wish to express an opinion as to the practicability of tapping the carbide as soon as it is formed. We will only mention that Mr. Price, in Newark, has, with a view of tapping the carbide, constructed and patented a new furnace, and that one of us (C.) has also devised a furnace for the same purpose.

Carbide of average quality (about five cubic feet of gas per pound) often has a reddish color, especially if it has been made with a current of high voltage. Carbide of bad quality is often grayish or blackish, or will show streaks of graphite. Pure carbide yields more than 5.90 cubic feet of gas per pound. It has, however, been found to be more economical to produce carbide that yields only about five cubic feet of gas per pound. Samples of carbide of different qualities contained :

TABLE I.

Cubic feet gas per pound.	Carbide. Per cent.	Free calcium oxide. Per cent.	Carbon. Per cent.	Other impurities. Per cent.
5.7	96.6	0.6	....	2.8
5.5	93.2	4.2	....	2.6
5.1	86.4	9.5	....	4.1
5.025	84.7	10.7	1.6	3.0
3.6	61.0	27.5	3.2	8.3
3.45	58.5	1.1	25.6	14.8

The upper part of a piece of carbide is often purer than the under part.

The coke to be used should not contain much ash. Our coke contains about seven per cent. of ash. The carbide obtained with a coke of from ten to eleven per cent. of ash was perceptibly inferior to that obtained with our usual coke. It was found impracticable to make a good quality of carbide with a coke of twenty-seven per cent. ash. It is well that there should not be more than ten per cent. of ash in the coke. The coke should be ground very fine, and it should pass through a fifty mesh sieve. The lime need not be as fine as the coke. The largest pieces should pass through a ten mesh sieve. If the lime is coarser the quality of the carbide becomes inferior. That the state of the pulverization of the lime is important, can be seen by a comparison of the average amount of gas per pound (4.97 cubic feet), obtained with unslacked lime (Table II), and that obtained with air slacked lime (5.27 cubic feet Table III). The unslacked lime was in several instances not quite as fine as the slacked lime. Unslacked lime is decidedly preferable to air slacked lime, as we will see afterwards.

The lime which we use contains one and one-half per cent. magnesia and one per cent. of other impurities. The anhydrous lime should contain ninety-five per cent. calcium oxide, and no more than five per cent. impurities. The presence of magnesia is especially detrimental to the production of carbide. We could not obtain a good quality of carbide with a lime in the following analysis: Insoluble, 0.24 per cent.; silica, 0.78 per cent.; ferric oxide and alumina, 0.68 per cent.; calcium oxide, 92.83 per cent.; magnesium oxide, 5.47 per cent. Further experiments showed that two and one-half per cent. of magnesia in

the mixture has a marked influence on the production. The lime used for making carbide should not contain over three per cent. of magnesia. That magnesia has such a bad influence upon the formation of carbide is probably due to its forming a veil between the carbon and the lime particles preventing their combination. Magnesia does not unite either with lime or with carbon. The latter fact was first shown by Moissan,<sup>1</sup> and our own experiments in this line fully confirm his results. The lime and the coke must be mixed very well or the carbide will be of inferior quality and there will be much coating. Besides the carbide some mixture remains in the furnace. More carbon than lime burns out or volatilizes in an open furnace. It is therefore necessary to add carbon to this mixture before using it again. The amount to be added is calculated from the result of an analysis of the mixture. If coke is added in the proper proportions, the unsmelted portion of the material can be returned at least three times into the furnace, and still yield good carbide. The impurities of the lime and the coke ashes remain as well in the carbide as in the residual mixture. It is therefore a good practice to add charcoal instead of coke to the mixture, so as not perceptibly to increase the amount of ash. The mixture that comes from the furnace is red hot and it will stay hot for days. It will lose a large amount of carbon if allowed to lay in heaps in the air. It is better to mix in the necessary amount of carbon and use the mixture at once again. One can also keep the mixture in air-tight sheet-iron tanks. If the lime has been unslacked the mixture cools much quicker and does not lose as much carbon after it has been taken from the furnace. In the case of slacked lime, water gas is probably formed in large amounts. The carbon pencils must be well cared for in order that they last for a long time. If sufficient coke is put in the mixture they are not attacked much at the end. They will shorten from 0.05 to 0.10 inch for every hour running. They become thinner for being exposed to the air when hot. They are mainly attacked after the electric current has been shut off, for if the furnace is working the gases from the arc come up around the carbons and shut the air off. In order to save the

<sup>1</sup> *Compt. Rend.*, 118, 506.

carbons best it is therefore well to keep the furnaces running with as little interruption as possible. In the closed furnace, which we have described, the carbons will be surrounded by non-oxidizing gases, which will save them materially. In the open furnaces in Spray we surround the carbons with a sheet iron cover that reaches from the carbon holder to within four inches of the bottom end of the carbons. This jacket is fastened with iron wires to the carbon holder. The space between the carbons and the jacket is packed with a mixture of coke and coal tar or pitch. This mixture is baked by surrounding the carbons and jacket with the red hot material that comes from the furnace or by placing them in a fire. The jacket will generally last as long as the carbons. One set of the carbons in an open furnace and with interrupted operations will last on an average about 100 hours. These figures hold good where a current of from 1700 to 2000 amperes is used. The voltage has no perceptible influence on the result. Working with say 1700 amperes and 100 volts and generating about 225 horse power, the production of carbide per hour can be reckoned to be easily eighty-five pounds, and one set of carbons can therefore make at least 8500 pounds of carbide, even in an open furnace. If the furnace is used continuously the carbons will last at least from 200 to 300 hours, and the cost of pencils for one ton of carbide will be about \$1.00.

The analytical part of our work has been very simple. After the piece of carbide has been broken open with a hammer, two or more samples, representing as nearly as possible the average quality of the carbide and of about eight ounces each, are taken. These samples are broken in pieces of about one-half inch in diameter and from two to three ounces are taken for one gas test. The material is put into a dry bottle of about one quart capacity, which is provided with a rubber stopper, through which two glass tubes pass. The one tube bears a stop cock and drop funnel, the other tube conducts the gas through a series of U tubes and then through a small gas-meter. The funnel is filled with water, and by opening the stop cock, water is allowed to drop slowly on the carbide. The acetylene gas is generated and is cooled in the U tubes before it passes to the

gas-meter. Much water vapor is condensed in the U tubes, for the gases generated in the bottle are hot. We make a correction for the temperature of the gas as it passes the gas-meter. We do not take into consideration the small amount of gas which passes through the gas-meter by the expansion of the gas in the bottle when the latter becomes hot, and because a part of the bottle becomes filled with water. The error arising herefrom is of no consequence, for the volume of the bottle is only one quart and the volume of the gas which passes from the gas-meter is from one-half to one cubic foot. The water, moreover becomes saturated with acetylene. Our figures show the amount of moist gas at the temperature of 60° F.

In order to determine the lime in the mixture, two and five-tenths grams are boiled with a slight excess of hydrochloric acid of known strength in a 250 cc. bottle. The bottle is cooled and filled up. The liquid is filtered and in fifty cc. of the filtrate the excess of acid is determined by titration. The coke is determined by boiling two grams of mixture with twenty-five cc. of twelve per cent. hydrochloric acid and filtering off the coke on a Gooch crucible. These methods do not make a claim to absolute accuracy, but they can be quickly executed and give a good estimate of the relation in which the coke and lime are present in the mixture, as the following figures show. The coke used for the original mixture contained 7.33 per cent. of ash. The coke that remained from the mixture that had been boiled with twelve per cent. hydrochloric acid contained six and eight-tenths per cent. of ash, and the coke which remained by the same treatment from a similar mixture that had been once in the furnace contained seven and eight-tenths per cent. ash. The amount of lime found in mixtures by titration and that found by gravimetric analysis varied only by from one-half to three-quarters per cent. when the small amount of magnesia in the lime was known and taken into consideration. In controlling the different runs we have proceeded as follows:

The carbide was weighed and the coating on it determined either by taking it off and weighing it or by estimating it on small and clean pieces. By deducting the weight of the coating from the weight of the piece of carbide we obtain the net yield

of carbide. The gas therein is determined, the figure accepted being the average of the result of the analyses of at least two samples. In order to determine the power used, we multiply the voltage by the amperage and divide the product by 746 to obtain the number of horse power generated by the dynamos. In order to make a more proper comparison we found it necessary to deduct the loss of voltage sustained in the carbon pencils. Our pencils were made in different factories and had a different resistance. We therefore determined the difference in voltage as indicated by the usual reading of our meter and the voltage at the end of the carbon pencils. We touch the end of each pencil alternately with an iron rod that is connected with the volt meter by a copper wire. We call net power the power generated by the dynamos less the average loss in the six carbon pencils. Our meters are placed in the primary circuit and we have not taken into account the losses of amperage in the transformers and those sustained by leakage. We have further found that the readings of our meters are about six per cent. higher than those of standard Weston meters. It may therefore be safely relied upon that all our estimates for the production of carbide per horse power are too low. The error is, however, in all cases in the same direction, so that it cannot have materially influenced our deductions, which are based upon a comparison of our results.

In the carbide there is also a considerable loss of voltage and therefore of power. We found, for example, sixty-five volts in the bottom cables and only fifty volts at the top of a two and a half feet high piece of carbide just under the arc. This makes a loss of six volts for each one foot of carbide. The average production during six to eight hours of continuous working is as large as that during two or three hours at the same power. It is, however, not advisable to make the carbide pieces higher than two and a half feet, since then the resistance of the carbide will begin to materially reduce the quantity of the production.

Taking into account the weight of the product, the time in which it has been produced and the number of horse power used, we calculate for each run the amount of pounds produced per horse

power in twenty-four hours. By multiplying these figures by the number of cubic feet of gas produced per pound we obtained the number of cubic feet of gas produced per horse power in twenty-four hours. In the following table we give the results of experiments wherein everything has been determined, wherein both unslacked and slacked lime have been used and voltage, amperage and duration of runs were varied. Since these results were obtained we have had many visitors from all parts of the country and for each party we have made a test run. The results of these runs have all confirmed our previous results, with one exception, which was due to the presence of five and a half per cent. magnesia in the lime.

TABLE II. UNSLACKED LIME.

Date.	Time of experiment. Hours.	Volts.	Amperes.	Loss of voltage in the pencils. Per cent.	Horse power.	Production in twenty-four hours includ- ing slag. Pounds.	Net produc- tion. Pounds.	Cubic feet of gas per hour.	Cubic feet of gas per horse power in twenty-four hours.
June 27th	2.50	100	1700	7.0	214	9.87	9.42	4.83	45.50
July 2nd	3.00	100	1666	8.0	205	10.34	9.76	5.25	51.24
" 1st	2.25	100	1700	10.0	205	10.66	10.10	4.66	47.06
June 24th	3.20	100	1600	7.0	214	11.50	10.73	4.93	52.90
" 28th	2.50	100	1700	10.0	205	11.70	11.10	4.75	52.72
July 18th	3.00	65	2000	5.0	165	9.63	9.15	4.95	45.29
" 19th	3.00	65	1900	5.0	158	10.40	9.62	4.83	46.46
" 5th	3.75	65	2000	5.0	165	8.38	8.15	5.40	44.01
" 9th	4.50	65	2000	5.0	165	9.50	9.05	4.99	45.16
Aug. 10th	6.00	65	1800	8.0	144	9.34	9.00	5.39	48.51
" 13th	6.00	65	1800	8.0	144	10.83	10.44	4.82	50.32
July 31st	7.00	75	1800	8.5	166	11.44	10.53	4.83	50.86
					Average,		9.75	4.97	48.33



TABLE III. AIR-SLACKED LIME.

Date.	Time of ex- periment.	Volts.	Amperes.	Loss of voltage in the pencils.	Horse power.	Production per horse power in twenty-four hours, includ- ing slag.	Net produc- tion.	Cubic feet of gas per pound.	Cubic feet of gas per horse power in twen- ty-four hours.
	Hours.			Per cent.		Pounds.	Pounds.		
June 25th	5.00	100	1700	7.0	214	8.34	7.96	5.30	42.19
" 29th	4.00	100	1700	10.0	205	8.78	8.34	4.98	41.53
" 19th	5.50	100	1700	7.0	214	9.25	...	4.89	....
" 22nd	4.00	100	1600	7.0	199	9.80	9.65	4.74	45.75
Aug. 14th	4.50	75	1700	7.0	159	7.88	7.13	5.50	39.22
July 12th	3.75	85	1800	3.5	198	...	6.33	5.55	35.13
" 26th	8.00	75	1800	5.0	172	8.40	7.23	5.33	38.54
" 12th	5.50	85	1775	8.0	185	...	7.32	5.32	38.94
" 6th	5.00	80	1020	3.0	200	8.78	8.16	5.11	41.70
" 23rd	3.00	65	1800	5.0	150	6.83	6.40	5.78	56.99
" 22nd	2.00	65	1800	5.0	150	7.13	6.40	5.62	35.97
" 22nd	2.00	65	1800	5.0	150	7.20	6.40	5.64	36.09
" 25th	9.00	65	1800	5.0	150	7.72	7.27	5.54	40.28
" 20th	4.00	65	1800	5.0	150	8.60	8.00	5.01	40.08
" 23rd	5.00	65	1800	5.0	150	9.02	8.00	5.07	40.56
" 24th	8.00	65	1800	5.0	150	9.30	8.03	4.97	39.91
Average,							7.51	5.27	39.52

It is obvious that the results obtained from unslacked lime are far better than those with air-slacked lime. This is undoubtedly due to a loss of power used in decomposing the hydrated lime. The unslacked lime used by us contained, after being ground, from five to nine per cent. of water. In practice it is necessary to use the mixture that comes from the furnace again. This mixture always contains some carbonate of lime, but if it be mixed when still hot with the necessary amount of carbon and put again into the furnace the lime has no opportunity to slack. The unslacked lime has the further advantage that it weighs less and is much less bulky, and that the mixtures made from it cool much faster than those made from slacked lime. The only disadvantages of unslacked lime are, that it must be ground and that mixtures made from it require more stoking if put into the furnace. The mixtures of unslacked lime can stand up against the sides of the furnace under a very steep incline and they can leave a hole all around the pencils. The mixture to be used should, on an average, contain 100 parts of

lime and sixty-four to sixty-five parts of carbon in order to obtain a carbide of about five cubic feet of gas per pound. If the voltage is increased to 100 it is better to take a little more carbon (100 lime and sixty-six to sixty-seven carbon). If the voltage is sixty-five or less, sixty-three to sixty-four parts of carbon are sufficient. If the amount of carbon is increased the carbide becomes purer, but there is often more coating.

The largest amount of gas per horse power is obtained if the carbide yields about five cubic feet of gas per pound. The yield of carbide in pounds varies inversely with the quality. In the following table we give the results of a series of experiments made with slacked lime and with a current of sixty-five volts and from 1700 to 2000 amperes. Several of these experiments have not been taken up in Table II, because the amount of slag on all the pieces of carbide has not been determined.

TABLE IV.

Date.	Production per horse power including slag. pounds.	Cubic feet gas per pound.
July 23rd	6.85	5.78
June 14th	7.10	5.80
July 22nd	7.13	5.62
" 22nd	7.20	5.64
" 25th	7.72	5.54
Aug. 14th	7.88	5.50
May 21st	8.10	5.20
" 22nd	8.30	5.10
July 26th	8.40	5.33
June 4th	8.46	5.52
July 20th	8.60	5.01
June 5th	8.76	4.94
May 28th	8.80	5.20
" 23rd	8.82	5.10
July 23rd	9.02	5.07
June 8th	9.06	5.10
" 24th	9.30	4.97
July 11th	9.30	4.33
Aug. 12th	9.44	4.51
May 31st	9.87	4.30
Aug. 8th	10.52	4.23

Carbide has been made successfully in Spray by the use of both the direct and the alternating current. We cannot express

an opinion as to what current can be used to the best advantage, for we are not able to compare results. All of the results communicated in this paper have been obtained by the use of the alternating current. That electrolysis plays a part in the carbide manufacturing process of Mr. Willson is therefore out of the question, and we do not need to use a furnace of the Moissan construction to prove this. It is not desirable to increase the amperage over 2000 if only six carbons of four inches square are used. The higher the amperage the greater the loss of voltage in the pencils and therewith that of power. The carbons will also last longer if the amperage is low, because they do not become so hot. Lastly we did not obtain as great a yield per horse power if the amperage was high and the voltage correspondingly low. We obtained the best yield of gas per horse power by using a current of 100 volts, which can be seen by comparing the average of the results given in Table II.

TABLE V.

	Volts.	Horse power.	No. of experiment.	Average cubic feet of gas per horse power in twenty-four hours.
Unslacked lime..	100	205-214	5	49.88
	65-75	144-165	7	47.23
Slacked lime.....	100	200-214	3	43.15
	75-85	159-100	5	38.71
	65	150	7	38.55

It must be taken into account that we measured the primary current and that the losses of amperage in the transformers probably have been higher when we did not use the highest voltage, *i. e.*, 100. We do not know in how far it would be advisable to increase the voltage over 100, since our dynamos cannot give us a current of more than 100 volts. We believe, however, that the heat yielded by an arc of 100 volts and from 1700 to 2000 amperes is about the largest amount to be profitably used for the production of carbide in one furnace with six pencils, as it is used in Spray. We base our assumption on the following facts: The quality of the carbide becomes better if the voltage decreases. We experienced some trouble in obtaining large carbide crystals with an arc of 100 volts and 1700 amperes, and in order to obtain a carbide that yields more than five cubic

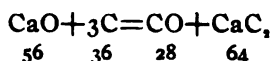
feet of gas per pound the mixture should contain an excess of carbon. If a current of 100 volts and 1700 amperes is used the furnace requires more attendance and stoking than if a lower power and especially a lower voltage is used. The higher the voltage the faster the pencils must be raised, for if the voltage is low (fifty or sixty-five) the carbide spreads out much more than if the voltage is high (100 volts). In the latter case the carbide builds up as a long thin piece and it is oftener necessary to empty the furnace. As to the time that one furnace should be used continuously, we wish to say that we did not perceive a difference in the quantity and quality of the product whether we ran three hours or from three to nine hours. We must, however, remark that in the case where we used 100 volts and 1700 amperes with mixtures of unslacked lime we could not continue running for much more than three hours because the construction of the furnace did not admit of raising the pencils quite three feet. With slacked lime we made also with this high power very satisfactory runs of five and five and a half hours. During the first hour the production is somewhat lower. It seems that more heat is lost probably for heating up the furnace.

The mixture used in all of the following experiments contained lime, 50.08 per cent., and coke,<sup>1</sup> 39.22 per cent. The current was of sixty-five volts and 1800 amperes, the loss of voltage in the pencils five per cent. and the net horse power 150.

TABLE VI.

Time of experiment. hours.	Production per hour in pounds.	Cubic feet of gas per pound.	Cubic feet of gas per hour.
1	37	5.63	208.31
2	40	5.62	224.80
2	40	5.64	225.60
3	40	5.78	237.20

We have now still to consider a very important question, namely, how much coke and lime are necessary to produce one pound of carbide. The formation of carbide taking place according to the following formula :



0.563 pound of carbon and 0.875 pound of calcium oxide are

<sup>1</sup> Of 92.17 per cent. of carbon.



TABLE VIII.

Number of experiment.	Mixture into the furnace.		Mixture out of the furnace.	
	CaO. Per cent.	C. Per cent.	CaO. Per cent.	C. Per cent.
1	54.70	36.32	57.01	36.89
2	54.51	34.18	57.29	33.36
3	56.23	36.46	57.00	35.62
4	55.66	36.51	55.47	35.02
5	59.70	34.43	58.16	32.94
6	56.65	36.09	55.60	32.61
7	55.44	36.32	54.93	31.09
8	50.64	34.43	51.81	34.29
9	52.08	29.39	52.09	28.90
10	49.34	33.85	41.45	28.27

The average figures of table VII are rather high, for where much coke and lime have been used this is certainly partly due to losses of material by weighing into and out of the furnace and also by insufficient stoking. In the King furnace, the under part of which shuts hermetically tight and excludes draught, and which is stoked mechanically, the amount of coke and lime necessary for making one pound of carbide will certainly be much reduced. In the figures given in table VII we have left the outside coating out of the calculation. In a plant where the acetylene gas is generated at once from the carbide it would pay to use this coating also for making gas. From table VII we see that a very large percentage of the mixture is not acted on by the arc. We have, however, reduced this amount to one-third of the mixture and could reduce it still more without either injuring the furnace, the quantity and quality of the carbide, and without increasing the amount of carbon and lime necessary for making one pound of carbide. In the furnace used in Spray the inside is square instead of octagonal and the dimensions are rather too large. We therefore feed more material into the furnace than is necessary.

Besides coke we have used several other carbonaceous materials for making carbide. We have used soft coal, anthracite, charcoal, pitch, tar, rosin, and asphalt, and obtained in all cases carbide. Most of these materials are not of sufficient importance to be taken into consideration and we will only add some words about the first three.

Charcoal, owing to its small percentage of ash, yields a very pure carbide. The only drawback, besides its price, is that it is so light that the gases carry it off to a considerable amount. It is therefore necessary to add from five to ten per cent. more carbon to the mixture if charcoal is used than if coke is used.

We used a soft coal which contained volatile matter 19.84 per cent. and ash 1.48. The mixture with soft coal gave a terrific blaze. The carbide was covered with a large amount of very porous slag in which there was much graphite. The average of results of two runs are : 6.41 pounds per horse power in twenty-four hours and 4.33 cubic feet of gas per pound, which equals 27.75 cubic feet of gas per horse power in twenty-four hours.

We used anthracite coal, which contained volatile matter 7.95 per cent. and ash 4.02 per cent. We made two runs with slacked and two with unslacked lime. There was no appreciable difference in the use of slacked and unslacked lime. The average result of the four runs was : 7.64 pounds per horse power in twenty-four hours and 4.03 cubic feet of gas per pound, which equals 30.79 cubic feet per horse power in twenty-four hours. These results are much lower than those obtained with coke. We can not therefore recommend the use of either anthracite or soft coal for making carbide. The superiority of coke and charcoal over anthracite is probably due to the porosity of the former materials, which must facilitate the volatilization of the carbon in the electric arc, which probably must precede the formation of carbide.

### ON THE ACTION OF WAGNER'S REAGENT UPON CAFFEINE AND A NEW METHOD FOR THE ESTIMATION OF CAFFEINE.

BY M. GOMBERG.

Received February 10, 1896.

THE use of iodine in potassium iodide as a general qualitative reagent for alkaloids dates as far back as 1839.<sup>1</sup> It was, however, R. Wagner<sup>2</sup> who first employed it for the quantitative estimation of vegetable bases, and this solution has since been known as Wagner's reagent. He based his con-

<sup>1</sup> Bouchardat: *Compt. Rend.*, 9, 475.

<sup>2</sup> *Dingl. poly. J.*, 161, 40; *Ztschr. anal. Chem.*, 1, 102.

clusion upon trials with solution of quinine and cinchonine, showing that under approximately similar conditions they always require the same amount of iodine for complete precipitation. Hence empirical factors could be established which would enable one to use a standard solution of iodine for the titration of all such alkaloids as form insoluble superiodides. The method, however, was not frequently employed, for the reason that there was no experimental proof as to the constancy of composition of the precipitates. Moreover, it was noticed that some of the precipitates give up a portion of their iodine to water, *i. e.*, they are not completely insoluble. Hence concordant results could not be obtained. Later, Schweissinger<sup>1</sup> applied this method to the estimation of strychnine and brucine. His results have led him to the conclusion that while the method is very satisfactory for strychnine, it is far from being so for brucine. Recently Kippenberger,<sup>2</sup> in his research upon the isolation and separation of alkaloids for toxicological purposes, has reviewed the subject of the action of Wagner's reagent upon alkaloids, and gives considerable prominence to this as one of the best methods for the estimation of the vegetable bases. His method of procedure was practically the same as that first proposed by Wagner. The alkaloid is dissolved in acidulated water, and to the solution a tenth or twentieth normal solution of iodine in potassium iodide is gradually added until all the alkaloid is precipitated and the supernatant liquid shows a slight excess of iodine. Instead of filtering and washing the precipitate, as was done by Wagner and Schweissinger, Kippenberger allows the precipitate to settle, and either decants or filters off an aliquot portion of the mother liquid for the estimation of iodine not taken up by the alkaloid. The estimation of iodine is always done by means of a standard solution of sodium thiosulphate.

It has been usually assumed, for reasons not entirely clear, that the composition of the precipitates is  $\text{Alk.HI.I.}$ , *i. e.*, diiodides of the hydriodides of the alkaloids are formed. Of the three atoms of iodine only two can be estimated directly by titration with sodium thiosulphate. The hydriodic acid is supposed to come from the potassium iodide, while the two "superio-

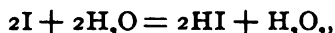
<sup>1</sup> *Arch. d. Pharm.*, 64, 615, 1885.

<sup>2</sup> *Ztschr. anal. Chem.*, 34, 317; 35, 10.



dine "atoms are furnished by the free iodine dissolved in the potassium iodide. The quantity of an alkaloid precipitated by a known volume of Wagner's reagent is calculated on this assumption,  $2I$  : molecular weight of alkaloid : : amount of iodine taken up :  $x$  = amount of alkaloid. Schweissinger found that the method of calculation agrees entirely with the theoretical figures for strychnine. Kippenberger has called into question the correctness of this mode of calculation. He, too, assumes that the composition of the precipitates is to be represented by the formula  $\text{Alk.HI.I}_3$ , but he claims that all three atoms of iodine are supplied by the free iodine, and none by the potassium iodide. Therefore the calculation of the amount of alkaloid precipitated is to be done, according to Kippenberger, by the use of the proportion,  $3I$  : molecular weight of alkaloid : : amount of iodine taken up :  $x$  = amount of alkaloid.

The hydriodic acid, it is supposed by Kippenberger, results from the interaction of iodine and water,



a reaction which is facilitated or induced by the avidity of the alkaloids to form insoluble periodides of the hydriodides. His reasons for assuming that such a peculiar reaction takes place under the simple conditions of precipitation, are too lengthy to be given here. All his arguments rest upon the assumption that all alkaloids form periodides of uniform composition,  $\text{Alk.HI.I}_3$ , and that the same alkaloid gives always the same periodide. Now, there is no reason, *a priori*, why this should be the case. Jörgenson's<sup>1</sup> extended researches show that different alkaloids, when treated under apparently the same conditions, give periodides of entirely different compositions. Thus, morphine gives with Wagner's reagent  $\text{Alk.HI.I}_3$ ;<sup>2</sup> codeine furnishes with excess of Wagner's reagent  $\text{Alk.HI.I}_4$ ; and caffeine, as will be shown, gives  $\text{Alk.HI.I}_3$ , etc. It is safe to say that not until we ascertain exactly the composition of the different periodides as produced under the conditions of titrations, will the use of Wagner's reagent for quantitative purposes be placed upon a sound basis.

<sup>1</sup> *J. prakt. Chem.*, 1870-78, [2], 2, 433, etc.

<sup>2</sup> Jörgenson, 1870 : *J. prakt. Chem.*, [2], 2, 438.

I have dwelt at such length upon this subject, because the method for the estimation of caffeine presently to be described, is based upon experimental evidence which is entirely contradictory to Kippenberger's conclusions. Whatever the cause may be with other alkaloids, his theory as to the production of hydriodic acid from iodine and water, does not hold good in the case of caffeine.

Wagner, in describing his method, gives a list of alkaloids which are completely precipitated by iodine solution, and also mentions that "caffeine, theobromine, piperine and urea are not precipitated at all."<sup>1</sup> His statement, so far at least as caffeine is concerned, has stood since then uncontradicted. It has found its way not only into standard treatises and text-books,<sup>2</sup> but even into periodical literature of recent date. As late as 1894, Kunze,<sup>3</sup> in reviewing the chemistry of caffeine and theobromine, calls attention to this peculiarity of the two alkaloids. The non-precipitation of caffeine by Wagner's reagent has come to be recognized as a distinguishing feature of this alkaloid from almost all other vegetable bases.

And yet this is entirely contrary to actual facts. Instead of forming an exception, caffeine conforms to all the requirements<sup>4</sup> necessary in the application of this test. It is well known that most of the alkaloids as such are insoluble, or only very slightly soluble in water; they require the presence of some acid for their complete solution. In other words, alkaloids in the form of their salts, are soluble in water. Whenever Wagner's reagent is applied for the precipitation of an alkaloid, it is always applied to a solution of some salt of it, preferably acidulated with sulphuric or hydrochloric acid. Therefore, even when strictly neutral salts of alkaloids are employed, there is still the possibility of the formation of hydriodic acid, or rather of the hydriodides of the alkaloid, as for instance,  $\text{Alk.HCl} + \text{KI} = \text{Alk.HI} + \text{KCl}$ .

<sup>1</sup> *Loc. cit.* 41.

<sup>2</sup> Prescott, *Organic Analysis*, p. 80; Allen, *Comm. Organic Analysis*, Vol. 3. (2). 481; Plückiger, *Reactions*, (Nagelvoort's Translation), p. 26; not affected by Wagner's reagent in either neutral or acid solutions; Dragendorff, 1888. *Ermittelung von Giften*, says that caffeine gives a dirty brown precipitate. From the text it is not improbable he used iodine in hydriodic acid.

<sup>3</sup> *Ztschr. anal. Chem.*, 33, 23.

<sup>4</sup> This test is perhaps most frequently made in a neutral solution, representing, as customary state, free caffeine and *normal salts* of other alkaloids.

The hydriodide thus produced is at once precipitated as a periodide. Now, it so happens that caffeine is tolerably soluble in water, and it has become customary to work with solutions of caffeine as a free alkaloid, and not in the form of its salts. The question as to whether solutions of free alkaloids are precipitated with Wagner's reagent has not, to my knowledge, been studied. My preliminary experiments in that direction show that at least some alkaloids (morphine, atropine, strychnine, etc.), are precipitated. I have not examined yet whether these periodides are identical in composition with those produced from the salts of the alkaloids. But so far as caffeine is concerned, it is true that a neutral solution of it gives no precipitate when treated with a solution of iodine in potassium iodide. When however the addition of Wagner's reagent is either followed or preceded by the addition of some dilute acid, there is at once thrown down a dark-reddish precipitate, remaining amorphous even on long standing.<sup>1</sup> The composition of this periodide is, as will be shown,  $C_8H_{10}N_4O_2 \cdot HI \cdot I_2$ . It was obtained for analysis in many different ways—by using either caffeine or iodine in excess, and by employing different acids. The periodide produced is, however, always of the same composition. The precipitates were allowed to settle, filtered by means of a pump, washed with water to remove the excess of potassium iodide, dried on porous plates, and finally in a *vacuum* over sulphuric acid.

I. This sample was obtained by slowly adding a solution of iodine in potassium iodide to a solution of caffeine acidulated with sulphuric acid. The iodine was added until the supernatant liquid was decidedly red. The whole was allowed to stand three hours, filtered, washed and dried as described above. The total iodine was estimated in the usual way, *i. e.*, by suspending a weighed sample in water, adding sulphurous acid solution, then silver nitrate and nitric acid; filtered, washed and dried. The "exterior" iodine, *i. e.*, the iodine not as hydriodic acid,

<sup>1</sup> Almost the same can be said of theobromine, making allowance for the difference of solubility of the alkaloid in water. A saturated solution of it (containing one part of theobromine to 1600 of water) gives no precipitate with Wagner's reagent, but on the addition of a drop of acid there separates in a short time a crystalline periodide. Contrary to usual statements, I find that theobromine in acid solutions gives a heavy precipitate with Wagner's reagent, of a peculiar dirty-blue color.

was estimated by direct titration with standard sodium thiosulphate.

0.2002 gram gave for total iodine 0.2785 gram AgI.

0.2358 " " " exterior " 0.1433 gram I.

II. This sample was obtained by adding to an acidulated solution of caffeine enough iodine to precipitate about one-half of the caffeine present.

0.2563 gram gave for total iodine 0.3591 gram AgI.

0.1659 " " " exterior " 0.0997 gram I.

III. A neutral solution of caffeine was mixed with an excess of Wagner's reagent, and to the mixture dilute sulphuric acid was gradually added so long as a precipitate was produced.

0.4039 gram gave for total iodine 0.5668 gram AgI.

0.1424 " " " exterior " 0.0866 gram I.

IV. Filtrates from I and III, on long standing, gave a deposit of dark-blue needle-like crystals, which were collected, washed and dried as before.

0.7884 gram gave for total iodine 1.1064 gram AgI.

0.4450 " " " exterior " 0.2685 gram I.

V. This was obtained by recrystallizing the amorphous precipitate from methyl alcohol.

0.2890 gram gave for exterior iodine 0.1756 gram I.

VI. Obtained by recrystallizing the amorphous periodide from hot ethyl acetate.

0.4807 gram gave for total iodine 0.6709 gram AgI.

0.2777 " " " exterior " 0.1622 gram I.

Calculated for	Per	Found.					
$C_8H_{10}N_4O_2 \cdot HI \cdot I_4$ .	cent.	I.	II.	III.	IV.	V.	VI.
Total iodine....	76.44	75.12	75.66	75.84	75.83	....	75.40
Exterior iodine.	61.15	60.79	60.11	60.81	60.34	60.76	60.22

When some of the periodide is treated with a solution of sulphur dioxide, and then extracted with chloroform, it furnishes unchanged caffeine.

The composition of this periodide of caffeine appears to be different from that described by Tilden,<sup>1</sup> which he obtained by exposing to sunlight an alcoholic solution of caffeine containing some hydriodic acid. The slow oxidation of the hydriodic acid

<sup>1</sup> *J. Chem. Soc.*, 18, 99, 1805.

furnished the iodine, and the compound thus obtained has the composition, according to Tilden,  $2(C_8H_{10}N_4O_2HI.I_2).3H_2O$ . It is a lower periodide than the one which is obtained when iodine dissolved in potassium iodide is directly added to caffeine, as the latter has the composition  $C_8H_{10}N_4O_2.HI.I_2$ . Tilden also mentions that by the addition of alcoholic iodine to a solution of caffeine in weak sulphuric or hydriodic acid, he obtained a deposition of black granules, which upon analysis furnished about seventy-five per cent. of total iodine. He says that it probably consists of a compound containing nine atoms of iodine. But there is hardly any doubt that he had the tetra-iodide of caffeine hydriodide.

*Properties.* When dry the periodide is a violet-blue amorphous powder melting at  $213^{\circ}C$ . When moist it rapidly loses iodine on exposure to air. It is permanent when dry and suffers but slight loss when heated to  $100^{\circ}C$ . Two grams heated for four hours at that temperature lost only 0.027 gram = 1.33 per cent. It loses but very little of its iodine when suspended in water, giving up enough iodine to saturate the liquid. The presence of potassium iodide in the water favors the liberation of iodine, but even then it is but slight. The periodide dissolves readily in alcohol, especially when heated, with considerable decomposition into the free base and iodine. It is more soluble in methyl alcohol and suffers less decomposition in that solvent. It can be obtained from methyl alcohol, on spontaneous evaporation of the solvent, in the form of beautiful crystals, with a metallic dark-bluish lustre. When examined under the microscope the crystals appear to consist of six-sided prisms. Ether, whether cold or warm, decomposes it but slightly. The periodide is insoluble in chloroform, carbon disulphide and benzene. It is soluble without decomposition in hot ethyl acetate, from which it separates on cooling as a dark granular crystalline deposit, which melts at  $215^{\circ}C$ .

*Limits of Precipitation.* Like most alkaloids, caffeine is precipitated by Wagner's reagent even from very dilute solutions of the base. Although not characteristic, it is yet as delicate a test for caffeine as we have. The limits of precipitation, under the influence of different acids, will appear from the following

table. The tests apply to one cc. of the solution mentioned, acidulated with two or three drops of the acid, and to this two drops of Wagner's reagent (twentieth normal) was added.

Dilution.	Sulphuric acid. Five per cent.	Hydrochloric acid. Five per cent.	Nitric acid. Five per cent.	Acetic acid. Five and fifty per cent.	Oxalic acid. Five per cent.	Tartaric acid. Ten per cent.	Citric acid. Ten per cent.
1 : 250	v. heavy.	v. heavy.	v. heavy.	none.	heavy.	slight.	faint.
1 : 1000	v. heavy.	v. heavy.	v. heavy.	.....	heavy.	v. sl.	none.
1 : 1500	heavy.	heavy.	heavy.	.....	sl.	none.	.....
1 : 3000	fair.	fair.	fair.	.....	faint.	.....	.....
1 : 5000	v. sl.	sl.	sl.	.....	.....	.....	.....
1 : 8000	v. sl.	sl.	sl.	.....	.....	.....	.....
1 : 10000	none.	v. sl.	v. sl.	.....	.....	.....	.....

#### ESTIMATION OF CAFFEINE.

All the methods for the estimation of caffeine depend upon the extraction of the alkaloid by an immiscible solvent from either a dry residue, or from its solution in water. But Spencer<sup>1</sup> has recently shown how difficult it is to remove the alkaloid from its solution in water. According to him, it is necessary to shake out the liquid at least seven times with chloroform, in order to remove caffeine quantitatively. It is usually stated that caffeine does not form any stable salts in a watery solution, and consequently it can be shaken out with immiscible solvents from either alkaline or acid solutions. But this is only relatively true, as will appear from the following illustrations. 1.0085 grams of caffeine were dissolved in sixty cc. of sulphuric acid (1 : 10), and this solution was repeatedly shaken out with chloroform, twenty-five cc. at a time.

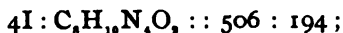
10 consecutive portions of chloroform gave a total of 0.3514 gram caffeine  
 3 additional " " " made a " " 0.4859 " "  
 3 more additional portions of " " " 0.5034 " "

The extreme delicacy of the test for caffeine by means of Wagner's reagent, has suggested the possibility of applying this reagent for the quantitative estimation of the alkaloid. Its successful application necessitates, of course, a solution of the alkaloid free from other substances that are precipitated by, or absorb iodine,—a condition requisite in the estimation of any base by

<sup>1</sup> *J. anal. Chem.*, 4, 390, 1890.

means of Wagner's reagent. This method gives very satisfactory results, as nearly theoretical as could be expected. I am indebted for the analytical data of the subjoined table to Mr. James W. Knox, holder of the Stearns' Fellowship in the School of Pharmacy. The method of procedure employed by us was practically the same as that used by Kippenberger. Definite volumes of acidulated solutions of caffeine were precipitated with a known volume of iodine in potassium iodide. After complete precipitation an aliquot portion of the supernatant liquid was obtained, either by decantation or filtration, and the excess of iodine was estimated by titrating against a tenth normal solution of sodium thiosulphate. The precipitation is best performed in a tall test-tube on foot, and the solution for titration is removed directly by immersing the end of the burette into the liquid and applying suction at the upper end. When it is desirable to filter off an aliquot portion, a filter of glass-wool and asbestos gives very satisfactory results.

We have tested the method on solutions of caffeine acidulated with sulphuric acid, the solutions being of different strengths, namely: containing 0.25 per cent. of caffeine, 0.50 per cent., 0.75 per cent., and 1.00 per cent., respectively. We have varied in different series of experiments the amounts of Wagner's reagent, employing just the theoretical quantities, a small and large excess above that, as well as quantities below those required by the theory. Columns I, II, III, and IV give the results obtained by allowing the solutions to stand for an hour before decanting an aliquot portion for titration; column V shows the results obtained when the liquid for titration was filtered off within five minutes after the addition of Wagner's reagent. The results are calculated on the basis that the periodide has the composition  $C_8H_{10}N_4O_8 \cdot HI \cdot I_2$ . The amount of alkalioid is calculated from the amount of iodine used up, by the formula,



*i. e.*, one part of iodine represents 0.3834 parts of caffeine. Or, one cc. tenth normal iodine = 0.00485 grams caffeine.

The results presented below show that the estimation of caffeine by this method is very exact. The best results are obtained

	I.			II.			III.			IV.			V.		
	Solution containing 0.25 per cent. of caffeine.			Solution containing 0.50 per cent. of caffeine.			Solution containing 0.75 per cent. of caffeine.			Solution containing 1.00 per cent. of caffeine.			Solution containing 0.50 per cent. of caffeine.		
Wagner's reagent employed.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.
Theoretical quantity + 2 cc.	0.0600	0.0591 0.0589	98.33	0.1200	0.1175 0.1175	97.82	0.1500	0.1481 0.1471	98.40	0.1200	0.1182 0.1179	98.38	0.1200	0.1154 0.1165	96.78
1½ theoretical quantity.	0.0750	0.0749 0.0749	99.88	0.1200	0.1191 0.1189	99.17	0.1500	0.1489 0.1485	99.13	0.1200	0.1191 0.1187	99.12	0.1200	0.1196 0.1197	99.75
Twice the theoretical quantity.	0.0500	0.0502 0.0506	100.80	0.0800	0.0805 0.0789	99.63	0.1200	0.1184	98.67	0.1100	0.1091 0.1091	99.18	0.0800	0.0802 0.0791	99.63
One-half of the theoretical quantity.	0.0750	0.0363 0.0363	48.40	0.1600	0.0794 0.0794	49.62	0.2250	0.1107	49.20	0.2000	0.1067 0.1067	53.35	0.1600	0.0791 0.0791	49.44



when iodine is in considerable excess, as is evident from the figures obtained where one and one-third and twice the theoretical quantities of Wagner's reagent were used. All the results in the table were obtained on solutions of caffeine acidulated with sulphuric acid, the acidulation being tolerably strong, about one cc. of the concentrated acid to fifty cc. of the liquid. Experiments upon the influence of the acid indicate that a large excess of sulphuric acid interferes to some extent with the reaction. The amount of recovered caffeine falls as low as ninety-five per cent. of the quantity taken, when four cc. of the concentrated acid to fifty cc. of the liquid are used. The results are also not very uniform and concordant. The fact that the precipitation of caffeine by Wagner's reagent is more delicate in presence of hydrochloric acid than any other acid would make it advisable to employ that acid in quantitative estimation of the base by iodine.

This method could easily be employed for the estimation of the alkaloid in caffeine-bearing drugs. Of course, it is necessary to have the final solution of the alkaloid in water as free as possible from other substances that may be precipitated by Wagner's reagent. The estimation of caffeine by this method is likely to give higher results than have hitherto been obtained. The following procedure is recommended.<sup>1</sup> The drug is thoroughly digested with water for some time, by the aid of heat, cooled, and made up to a definite volume, and filtered. An aliquot portion of the filtrate is treated with lead acetate, the precipitate allowed to settle, and filtered. The whole of the filtrate, or a given portion of it, is treated with hydrogen sulphide to remove the lead, and filtered. This filtrate, after boiling off the hydrogen sulphide, is divided into two equal portions, and each treated with a definite volume of the standard iodine solution,—the first portion without the addition of any mineral acid, the second with the addition of hydrochloric or sulphuric acid. After five to ten minutes' standing the excess of iodine is estimated in each of the two solutions, as described above. The first portion, containing no other but some acetic acid, serves to indicate whether the filtrate from the lead sulphide contains any other materials besides caffeine that are likely to be

<sup>1</sup> These directions are in part those given by Spencer, 1890: *J. anal. Chem.*, 4, 390.

precipitated by Wagner's reagent,—for caffeine itself is not precipitated by it even in presence of tolerably strong acetic acid. If any absorption of iodine be found in the first portion, then that quantity is to be subtracted from the amount of iodine taken up by the second portion; the difference represents the iodine used up in the formation of the periodide of caffeine. The amount thus used up, multiplied by 0.3834, gives the amount of caffeine in that particular portion of the liquid.

ANN ARBOR, MICHIGAN.

### ON THE FORMATION OF ANTIMONY CINNABAR.

BY J. H. LONG.

Received February 15, 1896.

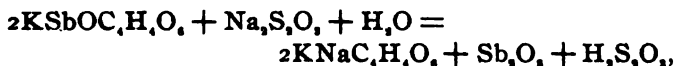
THE composition of the pigment known as antimony cinnabar has been stated by several different formulas, as may be seen by consulting the leading hand-books of chemistry. The substance was usually considered as a mixture of sulphide and oxide or as an oxysulphide with the formula  $\text{Sb}_2\text{S}_2\text{O}$ . The formula,  $\text{Sb}_2\text{S}_3$ , is found also in some of the older works, and Baubigny<sup>1</sup> has shown that this is undoubtedly the correct one. Experiments made by myself and described in this Journal, in February, 1895, led me to adopt the same formula.

The compound is usually prepared by boiling a solution of antimony chloride or tartrate with sodium thiosulphate or crude calcium thiosulphate. As obtained from the acid solution of the chloride, the product is not pure and not of constant composition, being frequently mixed with oxychloride. This mixture is a mechanical one and analysis made from it has no value in establishing a formula. The precipitate obtained by boiling a mixture of pure solutions of tartar emetic and sodium thiosulphate, on the other hand, has a constant composition, and numerous analyses I have made of it in the past year lead to the formula already given.<sup>2</sup>

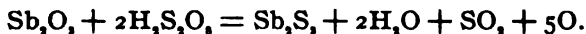
By analogy with other formulas established in the paper referred to I suggested there that the reaction between the tartrate and thiosulphate may be represented by this equation :

<sup>1</sup> *Compt. rend.*, October 22nd, 1894.

<sup>2</sup> *Loc. cit.*



the oxide and thiosulphate then acting on each other to form sulphide :



The oxygen and sulphur dioxide are not liberated as such but held as polythionates with the excess of thiosulphate used.

To throw further light on the reaction I have attempted the formation of the cinnabar by other methods. While the product is sulphide of antimony, it appears that it can be made with its characteristic color only by the decomposition of a thiosulphate. All attempts to obtain the true precipitate by action of hydrogen sulphide or alkali sulphides and sulphur dioxide on antimony solutions failed. The only body formed was the amorphous sulphide, often mixed with sulphur. On the other hand, by the action of a neutral or acid mixture of an antimony compound and a thiosulphate on each other, the cinnabar red product is the only one formed. If the mixture is made alkaline by the addition of a drop or two of ammonia water, no sulphide whatever precipitates. A small amount of hydrated oxide of antimony separates, but the decomposition of the thiosulphate is prevented. On the addition, now, of enough weak acid to neutralize the ammonia a yellow precipitate soon appears, but this speedily changes to deep bright red. The formation of the true cinnabar seems to begin by the appearance of a yellowish intermediate product, which is compatible with the above equations.

In this connection it is interesting to note the behavior of pure antimony trioxide with solutions of thiosulphate. The reaction of the latter with a soluble antimony compound is comparatively rapid, and experiments were made to show the action of the oxide under the same conditions. It was found that the latter, when added to a strong or weak neutral thiosulphate solution is unable to effect a decomposition, in the cold or by application of heat. When the mixture is boiled the oxide remains perfectly white. This is true even after heating in an autoclave under a pressure of eighteen atmospheres.

It was found, however, that with the addition of a little acid to the mixture of oxide and thiosulphate a reaction followed after a time, although it never became complete. In a series of experiments a constant weight, 0.576 gram, of the pure precipitated, washed, and dried oxide was taken and mixed with water and a constant weight of sodium thiosulphate in solution, in each case 0.992 gram of the salt. Definite volumes of half normal hydrochloric acid were then added and water enough to make the total volume fifty cc. in each case. The mixtures were made in small Erlenmeyer flasks, loosely stoppered, and were very frequently shaken. The amounts of hydrochloric taken are given in the table below. The reactions became apparent only after several minutes, and, after five hours, had advanced so far in the mixtures numbered one and two, that the products had become orange. The reactions in the other flasks were less marked, but later became strong. The mixtures were made on October 7th and were shaken many times daily through two months, in fact, as long as any change of color in them was noticed. On December third the amount of sulphide of antimony present was found by the method of Rivot, oxidation by chlorine after preliminary treatment with strong potassium hydroxide solution. The sulphur is found as sulphate and the amount of sulphide formed in each case is shown by the table.

No.	Amount of $\text{Sb}_2\text{O}_3$ .	$\text{Na}_2\text{S}_2\text{O}_3$ .	$\frac{\text{N}}{2}\text{HCl}$ .	$\text{H}_2\text{O}$ .	$\text{BaSO}_4$ found.	$\text{Sb}_2\text{O}_3$ converted.
1	0.576 gram.	0.992 gram	2 cc.	48 cc.	0.155 gram.	0.064 gram.
2	0.576 "	0.992 "	4 "	46 "	0.293 "	0.121 "
3	0.576 "	0.992 "	8 "	42 "	0.384 "	0.158 "
4	0.576 "	0.992 "	12 "	38 "	0.427 "	0.176 "
5	0.576 "	0.992 "	16 "	34 "	0.454 "	0.187 "

In mixtures one and two no evolution of sulphur dioxide could be detected by the odor or by tests, but in the others it was apparent, weak in 3 and strong in 4 and 5. No free sulphur was precipitated in any case, or at any rate could not be found in the final product. Although but a small part of the oxide was actually converted the color of the products in mixtures 1 and 2, was a deep cinnabar, and perfectly characteristic. The amounts of sulphide formed or of oxide converted are not

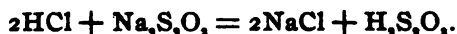
proportional to the volumes of acid used, and are much less than should be found on the assumption that the reaction begins by the production of antimony chloride from the oxide. If this were true, the sulphide formed by means of the soluble thiosulphate should increase with the acid taken. The reaction appears to take place between the oxide and thiosulphuric acid liberated by the hydrochloric acid, as was suggested by several experiments. In one case 0.500 gram of antimony oxide was treated with ten cc. of half normal hydrochloric acid and thirty cc. of water, as before, and allowed to stand twenty minutes, with frequent shaking. The mixture was then filtered and to the filtrate one gram of sodium thiosulphate in ten cc. of water was added. In a short time a precipitate of sulphur formed, perfectly light colored, showing the absence of even a trace of the antimony. The rapidity with which the thiosulphate was decomposed showed that the hydrochloric acid taken must be in the filtrate and not in the residue, as oxychloride for instance. Titration of the filtrate showed this in a similar case. In a second experiment the acid and thiosulphate, in amounts equal to those of the last experiment, were mixed, and after the lapse of one minute the now opalescent mixture was added to some antimony oxide. Although the reaction between the first substances had gone into its second stage, showing that the hydrochloric acid was now certainly in combination, a precipitation of antimony sulphide began almost immediately and in a short time the cinnabar color was distinct.

Thiosulphuric acid is usually spoken of as quite unstable, but Landolt has shown<sup>1</sup> that in dilute solutions it may exist many seconds, even minutes. The interval before precipitation is lengthened by dilution. If decomposition begins in presence of compounds of the heavy metals, a sulphide, sulphur dioxide, and polythionates may form. A large excess of thiosulphuric acid is necessary to complete the reaction in this manner, as suggested by the experiments of Vortmann.<sup>2</sup>

In experiment No. 1 of the table above the amount of hydrochloric acid taken is just one-eighth of that necessary to complete this reaction with the thiosulphate :

<sup>1</sup> *Ber. d. chem. Ges.*, 16, 2958.

<sup>2</sup> *Ber. d. chem. Ges.*, 22, 2307.

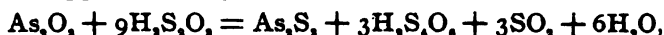


By full conversion enough acid would be liberated to complete the equation assumed at the beginning,



with the amounts of oxide and thiosulphate taken. It follows, therefore, that not over one-eighth of the antimony oxide taken should be found converted into sulphide, and the result of the experiment shows slightly less than this. According to this theory we should have 0.072 gram of oxide changed. The test shows 0.064 gram. In the second and following experiments the amount of oxide converted is relatively still less. The acid taken in the last experiment is sufficient to decompose all of the thiosulphate and thus permit the conversion of all of the oxide. But the result shows that slightly less than one-third the oxide has been changed. In the first experiment no escape of sulphur dioxide was noticed, while in the last it was quite marked and this fact has doubtless some connection with the low amount of sulphide formed. The reaction which takes place in a weak solution of thiosulphuric acid is evidently different from that in the strong solution, inasmuch as the greater portion of the sulphur seems to be given off as sulphide in the one case and as sulphur dioxide in the other.

In the somewhat similar reaction with arsenious oxide Vortmann<sup>1</sup> suggests this equation,



in which but one-sixth of the sulphur present is used to form sulphide. By increasing the amount of hydrochloric acid added to the thiosulphate the decomposition of the latter is hastened.

It is possible that after a time, with increased liberation of sulphur dioxide the formation of sulphide may be retarded, as was suggested by this experiment. I mixed half a gram of the antimony oxide with one gram of sodium thiosulphate in ten cc. of water, and added ten cc. of half-normal hydrochloric acid and thirty cc. of moderately strong solution of sulphur dioxide, free from air. By using water instead of the last solution, precipitation would appear in a few minutes, but in this case it was

<sup>1</sup> *Loc. cit.*

delayed several hours and then but a slight amount of yellowish product appeared. The thiosulphate is therefore protected from decomposition by the presence of the sulphur dioxide.

The cinnabar is easily formed from the oxychloride of antimony without addition of acid. Some recently precipitated and well washed oxychloride was mixed with water and thiosulphate solution of the strength used before. The characteristic color soon appeared and in a short time the whole product seemed to be cinnabar. The reaction is doubtless aided by the hydrochloric acid liberated by the decomposition of the oxychloride in presence of water. The acid in turn attacks the thiosulphate, and so the process becomes continuous and rapid. These reactions are all much hastened by application of heat and the quantitative relations are also altered, but, at a temperature of 20° C. thiosulphuric acid seems to be the active precipitating agent in the cases investigated.

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## PERHALIDES OF CAFFEINE.

BY M. GOMBERG.

Received February 25, 1896.

### I. INTRODUCTION.

THE formation of periodides by organic bases has been known as far back as 1839.<sup>1</sup> Their methods of preparation, their composition and properties have been subjects of investigation at different periods since then. Jörgensen,<sup>2</sup> in 1870, made a complete review of the subject, and has contributed a long list of new periodides. In 1887, Gunther<sup>3</sup> made a compilation of all the periodides known up to that time, and reported many new ones. More recently Prescott<sup>4</sup> offered a classification of all known periodides of both organic and inorganic bases, presenting at the same time a history of the principal advances in the study of the subject.

A strict separation of the periodides as such into those of alkylamines and those of pyridine and of its derivatives, seems

<sup>1</sup> Bouchardat, 1838: *Compt. Rend.*, 9, 475.

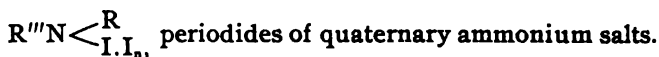
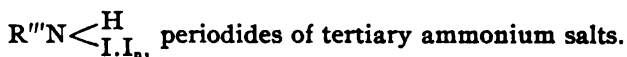
<sup>2</sup> *J. prakt. Chem.* [2], 2, 347, 433, 1870.

<sup>3</sup> *Ann. Chem.* (Liebig), 240, 66.

<sup>4</sup> This Journal, 17, 775.

hardly necessary. We know of no property, as to composition or stability, which is characteristic of one class of the periodides, and is not shared equally well by the other. At one time, Dittmar<sup>1</sup> thought to have found such a distinguishing reaction in the formation of chloriodides of the bases. According to him, it is only the bases of pyridine structure that are attacked by chloride of iodine, with the formation of chloriodides,  $\text{RNCl.I}$ . Yet it has been shown<sup>2</sup> previously to his report that this is not the case. Later, Ostermayer<sup>3</sup> reported the formation of such a chloriodide of caffeine, and recently Pictel and Krafft<sup>4</sup> obtained by the action of trichloride of iodine a similar chloriodide of trimethylamine.

All the periodides of primary, secondary, and tertiary ammonium salts, including those of pyridine and its derivatives, contain hydriodic acid as the salt forming acid, and the "periodine" is supposed to be linked to the iodine of this acid. The iodine of the acid, being linked directly to the nitrogen of the base, is not affected by reducing agents, such as sulphurous acid, sodium thiosulphate, nascent hydrogen, etc., while the "periodine" is readily attacked under such treatment, and yields hydriodic acid. The constitution of quaternary ammonium periodides, including those of the quaternary pyridine salts, is entirely similar to that of the tertiary class, the hydrogen of the acid being replaced by an alkyl. The following formulas will make this clear :



The organic bases are also capable of forming other halogen additive compounds, besides the simple periodides. These can be classified as follows :

1. Compounds wherein iodine or bromine is linked directly to the nitrogen without the intervention of a halogen acid, such as

<sup>1</sup> *Ber. d. chem. Ges.*, 18, 162, 1885.

<sup>2</sup> *J. Chem. Soc.*, 19, 145, 1866.

<sup>3</sup> *Ber. d. chem. Ges.*, 18, 2298, 1885.

<sup>4</sup> *Bull. Soc. Chim.* [3], 7, 72, 1892.



pyridine tetraiodide,  $C_5H_5N.I_4$ ,<sup>1</sup> quinoline tetrabromide,  $C_8H_7N.Br_4$ .<sup>2</sup>

2. Those obtained by the action of monochloride<sup>3</sup> and trichloride<sup>4</sup> of iodine upon bases. They contain both chlorine and iodine linked directly to the nitrogen. Their structure can be represented by the general formula  $R'''N \begin{smallmatrix} Cl \\ I \end{smallmatrix}$ . These compounds still retain the power of forming salts by union with acids, as  $(R'''NCl.I).HCl$ .

3. Periodides wherein the "periodine" is linked to another halogen not iodine. These are few in number, and are all on the quaternary ammonium type,  $R'''N \begin{smallmatrix} R \\ Br.I_n \end{smallmatrix}$ .

4. Periodides containing another acid<sup>5</sup> in addition to hydriodic acid, such as in herapathites, periodo selenites, phosphates, chlorides, etc. But as each contains hydriodic acid, Jörgensen legitimately infers that the "periodine" is in all probability linked to this acid and not to the other.

5. Perbromides of the hydrobromides of bases. Only very few of these have been reported, although it is well known that a great number of alkaloids are precipitated by bromine dissolved in hydrobromic acid. Pyridine,<sup>6</sup> quinoline,<sup>7</sup> and nicotine<sup>8</sup> form such perbromides.

All the perhalides of organic bases, so far reported, (except the simple periodides) can be referred to one of these five classes. And yet it can hardly be doubted that periodides and perbromides of other salts than hydriodides and hydrobromides respectively, are capable of existence. I have not been able to find any reports upon periodides in which either hydrochloric or hydrobromic acid has exactly the same function as hydriodic acid has in the simple periodides. Such derivatives can only be prepared when precautions are taken to strictly insure the absence of hydriodic acid during the preparation of the periodide,

<sup>1</sup> Dufert, *Monatsh. Chem.*, 4, 509, 1883; Prescott and Trowbridge: *This Journal*, 17, 865.

<sup>2</sup> Grimaux, 1882: *Bull. Soc. Chim.*, 38, 124.

<sup>3</sup> Dittmar, 1885: *Ber. d. chem. Ges.*, 18, 162.

<sup>4</sup> Pictel and Krafitt: *loc. cit.*, 72.

<sup>5</sup> Jörgensen, 1876: *J. prakt. Chem.* [2], 14, 213, 356; 15, 65.

<sup>6</sup> Grimaux: *Bull. Soc. Chim.*, 38, 127, 1882.

<sup>7</sup> *Ber. d. chem. Ges.*, 19, 2766, 1886.

<sup>8</sup> *Ann. Chem.* (Liebig), 131, 260.

and this has never been the case in the methods that have hitherto been employed for that purpose. In the following pages will be found a description of such periodides of caffeine, which have been obtained by a method different from those that have been described. The compounds have all been prepared by substituting chloroform for alcohol as the medium of reaction, thus eliminating the action of iodine upon alcohol at higher temperatures, and the subsequent formation of hydriodic acid. Not only periodides, but perbromides of similar composition and constitution have been prepared by this method. The method is, indeed, of very general application for such purposes. Periodides of hydrobromides and hydrochlorides of the following bases have thus been obtained: Quinine, quinidine, cinchonine, cinchonidine, strychnine, brucine, atropine and quinoline (of the hydrobromide only).

It has been said of the periodides that "if they contain, as their behavior has been interpreted to imply, for every atom of iodine that is linked to the base, a number of atoms of iodine linked only to iodine, they offer a striking example of the influence of a basal group upon iodine atoms to which it is not linked."<sup>1</sup> This naturally suggested the question, whether this influence is or is not proportional to the basal power of the group; in other words, is the number of iodine atoms thus attached under given conditions, an index of the basic power of the different bases? Again, we might ask whether the same influence is exerted in the same degree upon bromine. And furthermore, we might inquire, in how far does the nature of the halogen acid modify the influence of the base upon the "periodine," or "perbromine?" The following pages give an account of such a comparative study of perhalides of one base, caffeine.

## II. PERIODIDES OF CAFFEINE.

*Caffeine Hydriodide Diiodide*,  $C_8H_{10}N_4O_2 \cdot HI \cdot I_2$ .—Tilden reported in 1865,<sup>2</sup> that when a solution of caffeine in dilute alcohol, containing some hydriodic acid, is exposed to sunlight, there appears in a few days a deposit of beautiful crystals, with a metallic greenish appearance, unstable, readily decomposing

<sup>1</sup> Prescott, 1895: This Journal, 17, 775.

<sup>2</sup> J. Chem. Soc., 18, 99.

even at the water-bath heat. He assigned to the compound the formula  $(C_8H_{10}N_4O_7.HI.I_2) \cdot 3H_2O$ , and this agrees closely with the results of his analysis. In repeating the experiment, I find that under certain conditions a diiodide is formed, but the results of my analysis show no water of crystallization. Again, the diiodide is formed only when the formation of the crystals is tolerably rapid, as when the solution is kept in a warm place and exposed to direct light, conditions favoring oxidation of hydriodic acid. If, however, the liberation of iodine be very slow, yielding about a half gram of periodide in six or seven weeks, a tetraiodide is produced. The diiodide, obtained as above described, was filtered on a pump, washed with water containing some hydriodic acid, dried on porous plates and finally over sulphuric acid *in vacuo*. The samples were analyzed for total iodine and for the "periodine," or, as Tilden calls it, the "exterior" iodine. The first is estimated by suspending a weighed sample in water, treating with a solution of sulphur dioxide, then precipitating with silver nitrate and nitric acid. The "periodine" is estimated by titrating with a standard solution of sodium thiosulphate. The difference between the total and "exterior" iodine is that which corresponds to the hydriodic acid. Two independent samples thus prepared gave the following results :

	Calculated for $C_8H_{10}N_4O_7.HI.I_2$	Found.	
		I.	II.
Total iodine.....	66.06	65.12	64.29
Periodine .....	44.04	44.04	44.18

The diiodide consists of long hexagonal prisms, with a metallic greenish luster. It decomposes readily when moist, but is quite stable when dry. When suspended in water the crystals lose their luster and become coated with a brown-red layer of the tetraiodide. It is soluble in warm alcohol with decomposition, insoluble in ether and chloroform. It melts at  $171^{\circ} C$ .

*Caffeine Hydriodide Tetraiodide*,  $C_8H_{10}N_4O_7.HI.I_4$ .—This is the periodide which caffeine usually forms when it forms any at all, except as above described. It is the most stable periodide of caffeine, and is formed under many different conditions, in both the amorphous and crystalline state. It has been obtained by the following methods :

1. When a solution of caffeine is treated with a solution of iodine in potassium iodide (Wagner's reagent), there is no visible reaction. On the addition of some mineral acid, a heavy amorphous dark-red precipitate is at once thrown down. The precipitation of caffeine in this way is quantitative, and forms the basis of a method for the estimation of caffeine.<sup>1</sup> The composition of this precipitate is, as I have fully described,<sup>2</sup>  $C_8H_{10}N_4O_9.HI.I_4$ . It was obtained for analysis in many different ways by varying the relative quantities of the reagents employed, but it has always proven to be of the same composition. The samples for analysis were obtained by filtering the amorphous precipitate on a pump, washing with water to remove the potassium salts, drying rapidly on porous plates, and finally *in vacuo* over sulphuric acid. The following are the results of analysis :

	Calculated for $C_8H_{10}N_4O_9.HI.I_4$	I.	Found. II.	III.	IV.
Total iodine.....	76.43	75.12	75.66	75.84	....
Periodine.....	61.15	60.79	60.11	60.81	60.76

2. When caffeine is dissolved in chloroform and is treated with a solution of iodine also in chloroform, no formation of any periodide could be noticed, even when the mixture is allowed to stand for weeks. If into this solution dry hydriodic acid gas be now passed, there is at once precipitated an amorphous dark-red periodide, identical in composition with that described under 1. Upon analysis it gave the following figures :

	Per cent.
Total iodine .....	75.14
Periodine .....	60.23

3. When a solution of caffeine in hydriodic acid is exposed to sunlight, but the liberation of iodine is hindered either by low temperature, or the presence of some reducing agents in the solution, then the crystals that are formed have the composition of the tetraiodide, and not that of diiodide. They also have a different appearance, being short prisms of a deep blue color. Several samples obtained in this way furnished the following figures :

<sup>1</sup> This Journal, 18, 331.

<sup>2</sup> Loc. cit.

	I.	II.	III.	IV.
Total iodine .....	....	....	....	75.11
Periodine .....	60.26	59.86	59.75	60.60

4. When either caffeine hydrobromide dibromide or tetrabromide is triturated with a solution of potassium iodide in water, there is again produced the same amorphous periodide. It gives upon analyses 59.90 per cent. of "exterior" iodine.

These four different methods show the great tendency of caffeine to form the higher periodide, which is apparently more stable than the the diiodide. Weak base as it is, caffeine readily forms a higher periodide than is produced under similar conditions by many other organic bases.

*Properties.*—The periodide in the amorphous state and when dry, is of a dark blue-red color. It is quite stable when dry, and can be heated at 100° C. for many days without any appreciable loss of iodine. When moist it readily gives off iodine. Suspended in water, it gives up sufficient iodine to saturate the liquid, and after that remains unchanged. A solution of potassium iodide removes only a little more iodine than pure water alone. The periodide cannot be recrystallized from alcohol without considerable decomposition into caffeine and iodine. It is more soluble in methyl alcohol, and if not too much heat be used in dissolving it, the periodide can be obtained unchanged on spontaneous evaporation of the alcohol in the form of dark-blue needles. Ethyl acetate is, however, the best solvent for this periodide, as the latter dissolves in acetic ether without decomposition, even when heated. On cooling, the periodide separates in fine compact crystals. It is insoluble in chloroform, ether, benzene and carbon disulphide. It melts at 215° C.

*Caffeine Hydrobromide Tetraiodide*,  $C_8H_{10}N_4O_6 \cdot HBr \cdot I_4$ .—Caffeine forms with hydrobromic acid a salt of the following composition,  $C_8H_{10}N_4O_6 \cdot HBr + 2H_2O$ .<sup>1</sup> The salt can best be obtained in the pure state by passing dry hydrobromic acid gas into a solution of caffeine in chloroform. The white crystalline precipitate is filtered, washed with chloroform and dried in an atmosphere free from moisture. Thus prepared it has the composition  $C_8H_{10}N_4O_6 \cdot HBr$ . The periodide of this hydrobromide

<sup>1</sup> R. Schmidt, 1881: *Ber. d. chem. Ges.*, 14, 815.

can only be prepared in the absence of other halogen acids, especially of hydriodic acid. Therefore the addition of iodine as a solution in potassium iodide, to a solution of caffeine hydrobromide, is out of the question, as in such a case the periodide of the hydriodic acid will be formed. Nor can alcohol be successfully employed as a solvent for iodine, because this will furnish hydriodic acid, and also because the periodide of the hydrobromide itself is more or less dissociated by alcohol. This periodide is, however, readily obtained when a slow stream of dry hydrobromic acid gas is led into a solution of caffeine and iodine in chloroform. The addition of the acid must be very slow, and care must be taken to have the iodine in excess, otherwise the pure hydrobromide, or lower periodides of it will be thrown down together with the tetraiodide. In such cases redigesting the mixed periodides in a fresh solution of iodine in chloroform converts them into the tetraiodide. Further digestion shows no absorption of iodine. The periodide is filtered, washed with chloroform to remove the excess of caffeine or iodine, as the case may be, dried on porous plates, and finally in a desiccator. The "exterior" iodine is estimated by titration with sodium thiosulphate. The bromine is found by subtracting from the total mixture of silver halides, as obtained by precipitation with silver nitrate, the quantity of silver iodide corresponding to the "periodine" as found by titration. This difference represents the amount of silver bromide. The accuracy of this method was tested in several instances by actually estimating the amount of silver as such in the precipitate of the mixed halides, and from this the relative proportions of the two halogens were calculated.

The analysis of several samples furnished the following figures:

	Calculated for $C_8H_{10}N_4O_2 \cdot HBr \cdot I_4$	I.	Found. II.	III.
Iodine .....	64.79	63.56	63.91	62.28
Hydrobromine .....	10.37	9.63	....	....

This periodide is usually obtained as an amorphous powder. But when the addition of hydrobromic acid is very slow, it can be obtained in microscopic crystals. It is of a dark-brown chocolate color, and melts at  $183^\circ \text{C}$ . It is decomposed by water

but slowly, more readily, however, than the corresponding hydriodide. It dissolves readily in alcohol, with considerable decomposition. It is more soluble in methyl than in ethyl alcohol, and also with less decomposition. On evaporating the methyl alcohol the tetraiodide can be obtained in brown crystals. It can also be recrystallized from ethyl acetate. Ether removes considerable iodine, and chloroform, hot or cold, does not affect it. On exposure to air the periodide gradually, but slowly, loses iodine, and hardly any if protected from moisture. By heating to 100° C. the iodine can be driven off completely. Thus this periodide is in all respects a less stable compound than the corresponding tetraiodide of caffeine hydriodide.

*Caffeine Hydrochloride Diiodide*,  $C_8H_{10}N_4O_2 \cdot HCl \cdot I_2$ .—Caffeine is capable of uniting with hydrochloric acid under certain conditions, and the salts have been assigned the following composition:  $C_8H_{10}N_4O_2 \cdot HCl + 2H_2O$  and  $C_8H_{10}N_4O_2 \cdot 2HCl$ .<sup>1</sup> Pure caffeine hydrochloride is however much easier obtained by simply passing dry hydrochloric acid gas into a solution of caffeine in chloroform. Washed with chloroform, and dried in an atmosphere free of moisture, it has the composition  $C_8H_{10}N_4O_2 \cdot HCl$ .

Compounds containing both chlorine and iodine have been reported before. Tilden<sup>2</sup> obtained a chloriodide of caffeine by the action of chloride of iodine upon caffeine. It combines with acids to form salts, and Tilden assigns to it the composition  $C_8H_{10}N_4O_2 \cdot Cl \cdot I$ , or  $C_8H_{10}N_4O_2 \cdot ICl \cdot HCl$ . But from Dittmar's<sup>3</sup> latest reports upon the action of chloride of iodine upon bases in general, the caffeine compound most likely has the composition as expressed by the second formula. The periodide presently to be described is however the first periodide of caffeine wherein the hydrochloric acid has the same function in the molecule as hydriodic acid usually has in the other periodides. And, to my knowledge, this is the first periodide of its kind ever reported of any base. The "periodine" in the hydrobromide is linked to the nitrogen through the bromine, in the periodides of the hydrochloride it is linked through the chlorine.

Caffeine hydrochloride diiodide is prepared by passing hydro-

<sup>1</sup> E. Schmidt: *Ber. d. chem. Ges.*, 14, 815.

<sup>2</sup> *J. Chem. Soc.*, 19, 145.

<sup>3</sup> *Ber. d. chem. Ges.*, 18, 162.

chloric acid gas into a solution of caffeine into chloroform containing iodine. The periodide separates almost immediately in the form of compact, small, crystalline granules, of light-brown to brown color. The samples for analysis were prepared similarly to the other periodides described, and furnished the following results :

	Calculated for $C_8H_{10}N_4O_9.HCl.I_2$	I.	II.	Found. III.	IV.	V.
I .....	52.34	53.38	52.44	53.44	52.88	53.64
HCl.....	7.53	7.40	....	....	....	....

The periodide is of a light brown color, crystalline, and melts at  $165^{\circ}C$ . Digested with excess of iodine for several days, it refuses to take up any more iodine. It is rapidly decomposed by water. Both methyl and ethyl alcohol remove the iodine readily and completely, leaving a white powder of caffeine hydrochloride. The periodide is soluble in ethyl acetate with partial decomposition, is insoluble in either cold or hot chloroform, and is not affected by ether. Exposed over potassium hydroxide in a desiccator it remains unchanged, but slowly loses iodine when exposed to air not freed from moisture. On heating to  $100^{\circ}C$ . all the iodine is driven off. Thus in all its properties it is even less stable than the periodide of caffeine hydrobromide.

### III. PERBROMIDES OF CAFFEINE.

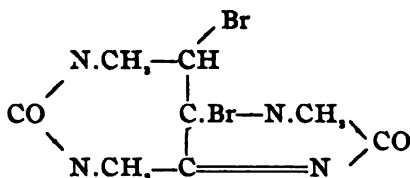
The action of bromine upon caffeine has been the subject of investigation many times. When pure bromine is employed, in absence of water, the final action of bromine results in the formation of a substitution product, bromocaffeine,  $C_8H_7BrN_4O_2$ .<sup>1</sup> In presence of water the action of bromine upon caffeine is for the most part that of an oxidizing agent, as has been shown by Maly and Hinteregger.<sup>2</sup> But under whatever conditions bromine is added to a solution of caffeine or to the dry base, be it as bromine-water or pure bromine, there is at first thrown down an orange-red to a brick-red precipitate. According to Maly and Hinteregger's results of analysis it is a mere addition product, caffeine dibromide, and E. Fisher<sup>3</sup> expresses the same opinion. The constitution of the compound is presumably this :

<sup>1</sup> O. Schultzen : *Ztschr. Chem.*, 1867, 614 ; E. Fisher : *Ann. Chem. (Liebig)*, 215, 264.

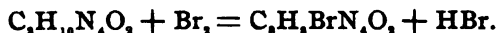
<sup>2</sup> *Monatsh. Chem.*, 3, 85, 1882.

<sup>3</sup> *Ann. Chem. (Liebig)*, 215, 264.





I have subjected caffeine to the action of bromine under many varied conditions, but in no case have I been able to obtain this addition product. Indeed, as will be shown, its existence is entirely hypothetical. Although Maly and Hinteregger's results of analysis agree with the theoretical figures of the formula assigned by them to the compound, yet their method of obtaining and purifying the substance for analysis is such, as to preclude the reliability of the results of analysis. The addition compound will be shown to have the composition  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_6\text{.HBr.Br}_2$ , and not  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_6\text{.Br}_2$ . This perbromide loses a portion of its bromide quite readily; consequently, it must be analyzed, or at least protected from exposure, as soon as dry. Hence, Maly and Hinteregger's results, obtained upon samples which have been previously exposed over lime in a desiccator for several weeks, cannot furnish reliable data as to the composition of the original substance. Just as under the action of iodine in presence of hydriodic acid, caffeine exhibits a great tendency to form higher periodides, so under the action of bromine it always forms the tetrabromide of the hydrobromide. This takes place whether hydrobromic acid be added as such or not. When none is added, some hydrobromic acid is produced, either by the action of bromine upon water or by the direct action upon caffeine,



It is only under special conditions that lower perbromides of caffeine are obtained.

*Caffeine Hydrobromide Tetrabromide*,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_6\text{.HBr.Br}_4$ .—Whenever bromine is allowed to act upon caffeine, this perbromide is one of the first products of the reaction, if not the only one. It is produced in presence or in absence of hydrobromic acid, in presence of water, of chloroform, or when pure bromine is employed.

1. *In Presence of Water.*—When bromine-water is gradually added to a solution of caffeine acidulated with hydrobromic acid, there is produced a yellow amorphous precipitate, which becomes darker and more compact; also, if the addition of bromine be very gradual, the precipitate becomes crystalline. The same compound is however obtained easier, and more crystalline, by the following method of procedure: A stream of carbon dioxide is allowed to bubble through a column of pure bromine, and the fumes of the latter, greatly diluted with carbon dioxide, are carried into a solution of caffeine containing some hydrobromic acid. As the bromine first reaches the solution, the bubble of the gas becomes surrounded with a pale-yellow film, which soon grows darker, and the product finally settles to the bottom as an orange-red crystalline deposit, consisting of distinct small prisms. If the bromine fumes be passed into the solution too rapidly, the resulting product is amorphous. One gram of caffeine furnishes by this method two and three-tenths grams of the perbromide, which is about eighty per cent. of the theoretical value. The samples for analysis were filtered, by the use of a pump, washed with weak bromine-water, and dried by pressing on very porous plates. When dry, in about two hours, the upper layer of the mass is removed, and the rest is put away in small glass-stoppered bottles, where it remains unchanged for weeks. The washing and drying should not be prolonged any more than is necessary, as the compound loses bromine readily, especially when moist and exposed to open air. The samples were analyzed for the "exterior" bromine and for total bromine. The first was estimated by suspending a weighed quantity of the sample in a solution of potassium iodide, and the iodine thus liberated is titrated with a standard solution of sodium thiosulphate. The total bromine was estimated by precipitation with silver nitrate, in a manner entirely similar to that employed in the estimation of total iodine in the periodides. Several samples, prepared separately, gave the following results:

	Calculated for $C_8H_{10}N_4O_2 \cdot HBr \cdot Br_4$	Found.					
		I.	II.	III.	IV.	V.	VI.
Total bromine.....	67.23	67.37	65.74	67.89	.....	.....	.....
"Perbromine" .....	53.78	54.00	52.07	54.04	54.18	53.11	52.58

The addition of hydrochloric acid or sulphuric acid, instead of

the hydrobromic, does not give perbromides of salts of these acids, but the same perbromide of the hydrobromide of caffeine.

The same product is obtained even if no acid whatever be added. Thus, when fumes of bromine, absolutely free from hydrobromic acid, are passed into a solution of caffeine, there appears after a short time a precipitate of exactly the same appearance and composition as the perbromide described above. The precipitation is much slower than when hydrobromic acid is present, nor is the yield so large. One gram of caffeine yields from two-tenths to three-tenths gram of the perbromide, which is only about eight to ten per cent. of the theoretical value. Samples for analysis, prepared as previously described, gave the following figures :

	I.	II.	III.
Total bromine.....	65.92	....	....
" Perbromine " .....	52.57	53.27	54.75

This is undoubtedly the same perbromide as obtained in presence of hydrobromic acid. The slow precipitation and the small yield point conclusively that a large portion of the caffeine suffers some other changes, namely, those of oxidation and substitution, either of which would give rise to hydrobromic acid. The acid thus produced would at once tend to form the perbromide of the hydrobromide of caffeine. Filtrates from such perbromides invariably give within a short time bulky precipitates of the white bromocaffeine,  $C_8H_7BrN_4O_2$ .

Great precautions were taken to insure the absence of hydrobromic acid in the bromine used. For this purpose the latter was washed with a solution of sodium hydroxide, then with sulphuric acid, and finally kept under a column of sulphuric acid saturated with silver sulphate. In some experiments the fumes were also passed through a second bottle containing sulphuric acid and silver sulphate. But the perbromide of the hydrobromide was always produced even under these conditions.

*Properties.*—The perbromide consists of small orange-red prismatic crystals. It melts sharply at  $170^{\circ}C$ . with previous decomposition into the dibromide, and finally decomposes completely. When suspended in water, it gives up some of its bromine, and then gradually and slowly changes into the white bromocaffeine.

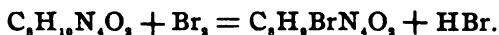
Two grams of the perbromide change in this way completely in about one week. When spread out on plates and exposed to air for about twenty-four hours, it loses two atoms of bromine, leaving a more stable residue, the corresponding dibromide, which suffers very little loss of bromine on further exposure. The tetrabromide is quite soluble in alcohol, more so when warm, from which it separates, on cooling, in the form of a lower perbromide mixed with some pure caffeine. Methyl alcohol dissolves the tetrabromide very readily, with the production of large quantities of formic aldehyde, and almost complete reduction of the bromine. It dissolves in warm ethyl acetate, and this on evaporation furnishes yellow crystals of a lower perbromide. The perbromide is only slightly soluble in either hot or cold chloroform. Ether removes two atoms of bromine, leaving the yellow dibromide of caffeine hydrobromide. When heated, the tetrabromide loses a portion of its bromine, and finally changes into bromocaffeine, especially at a higher temperature, about  $160^{\circ}$ – $170^{\circ}$  C.

2. *Action of Bromine in the absence of Water.*—When a weak solution of bromine in chloroform is added to a solution of dry caffeine in the same solvent, there appears after some hours' standing a deposit of flaky crystals. With strong solutions of bromine the formation of crystals begins to take place at once, the amount constantly increasing. The mother liquids, after filtering off the crystals, give new crops of the same compound. It was the compound thus produced that was analyzed by Maly and Hinteregger, after being allowed to stand several weeks over lime. The perbromide was filtered, washed with chloroform containing bromine, and dried on porous plates. It was found to be identical in composition with the one obtained similarly but with the previous addition of hydrobromic acid gas also dissolved in chloroform. The analyses I. and II. are upon samples obtained without the use of hydrobromic acid, while analyses III. and IV. are upon samples prepared with the addition of the acid.

	I.	II.	III.	IV.
Total bromine.....	68.25	....	....	....
Perbromine .....	52.25	54.79	54.40	52.82

The perbromide thus obtained is entirely identical in its behavior towards different reagents and solvents with that obtained by the action of bromine upon caffeine in presence of water. It melts at  $170^{\circ}\text{C}$ .

The question may be asked, whence comes the hydrobromic acid that furnishes the hydrobromide of the base? The bromine used in all these experiments was carefully freed from any hydrobromic acid that might have been originally present. The chloroform also was dehydrated for several days over fused calcium chloride, and finally carefully distilled. Blank experiments with absolutely dry chloroform (distilled over phosphorus pentoxide) have established that there is practically no absorption of bromine by the chloroform, when a three per cent. solution of the halogen in that liquid is exposed to light for several days. Therefore, the hydrobromic acid in the reaction could not have been produced from the substituting action of bromine upon chloroform, a reaction which takes place only at higher temperatures. From the rapid formation of the perbromide when strong solutions of bromine are used, it may reasonably be assumed that at least a portion of the hydrobromic acid, if not all of it, must have been produced directly as one of the products of the substituting action of bromine upon caffeine itself, thus:



Additional proof to this theory is lent by the fact that by fractional precipitation, products are eventually obtained which give somewhat higher results for total bromine, while the "perbromine" is about the same. This would point towards the formation of  $\text{C}_8\text{H}_8\text{BrN}_4\text{O}_6 \cdot \text{HBr} \cdot \text{Br}_2$ , a compound, the description of which will be given further on. The last crops of crystals show also a lower melting point,  $150^{\circ}$ – $156^{\circ}\text{C}$ .; and when the crystals are suspended in water and treated with sulphurous acid, they yield besides caffeine an insoluble precipitate of the white bromo-caffeine.

3. *Action of Pure Bromine.*—When dry caffeine is slowly added to pure bromine the first portions go into solution, but further addition produces a dark-red insoluble mass, which was supposed by Maly and Hinteregger, and by E. Fisher, to be the

caffeine dibromide,  $C_8H_{10}N_4O_2.Br_2$ . It is, however, not that, but the same tetrabromide of caffeine hydrobromide just described, mixed with a similar perbromide of bromocaffeine.

Dry caffeine was slowly added to a large excess of bromine free from hydrobromic acid, and the mixture was allowed to stand six hours. The thick dark mass was then spread out on porous plates, and allowed to remain over lime for three days. It was then divided into three portions: (*a*) was analyzed at once, (*b*) was washed with chloroform, and (*c*) was again redigested in pure bromine. The results of analysis are as follows:

	<i>a.</i>	<i>b.</i>	<i>c.</i>
Total bromine .....	69.45	68.50	68.03
Perbromine .....	53.88	54.60	53.07

On treatment with reducing agents there is left a slight residue of the insoluble bromocaffeine, and its formation would readily account for the high results of total bromine. The reaction then in this case is the same as when chloroform is employed. A small portion of the caffeine is at once attacked by the bromine and forms bromocaffeine and hydrobromic acid. The acid at once unites with the unchanged caffeine and forms the insoluble perbromide, thus protecting it against further direct action of bromine; then the bromocaffeine is in its turn slowly changed into a similar perbromide.

So far, then, as experimental evidence goes, the caffeine dibromide,  $C_8H_{10}N_4O_2.Br_2$ , is entirely hypothetical. It may still be said that the evidence does not exclude the possibility that only two atoms of bromine go to form the perbromide, while the other two atoms are retained by caffeine through the unsaturated linking between the two carbon atoms. Against this view there stands the simple fact that iodine, even in dilute solutions in water, forms the analogous tetraiodide. It is hardly probable that iodine would attach itself so readily to carbon. Then again, no assimilation of either bromine or iodine by caffeine takes place unless some acid be present. Hence, the constitution of this perbromide must be analogous to that of the periodide, *i. e.*, it is a pure and simple caffeine hydrobromide tetrabromide.

*Caffeine Hydrobromide Dibromide*,  $C_8H_{10}N_4O_2.HBr.Br_2$ .—When the tetrabromide is exposed to air it loses bromine, and after

twenty-four to forty hours there is left a yellow amorphous powder, which is tolerably stable and can be further exposed for many days without any appreciable loss of bromine. The results of analysis show this to be caffeine hydrobromide dibromide. The same compound is obtained by treating the tetrabromide with anhydrous ether. Samples of the tetrabromide were finely powdered under ether, and the digestion with ether was continued until fresh portions of the solvent showed no coloration when added to the perbromide. The yellow residue was filtered, washed with ether, and dried by exposure. It is identical in composition and properties with that obtained by simple exposure of the tetrabromide. Analyses I, II, and III are upon samples obtained by exposing the tetrabromide to air. Analyses IV and V are upon samples obtained by treatment with ether.

	Calculated for $C_8H_{10}N_4O_6 \cdot HBr \cdot Br_2$	I.	II.	Found. III.	IV.	V.
Total bromine...	55.17	....	53.45	....	54.99	....
Perbromine .....	36.78	36.48	35.50	35.93	36.87	35.83

The dibromide ranges in color from pale-yellow to a decided yellow. It is amorphous, and melts at  $170^\circ$  C. When suspended in water it turns orange-red, and, as analysis shows, is changed into the tetrabromide. It is soluble in ethyl alcohol with less decomposition than the higher perbromide. On cooling the alcohol it separates in distinct tetrahedral crystals, containing less bromine than the original compound (total = 42.50 per cent., and "exterior" bromine 27.8 per cent.) Methyl alcohol dissolves the dibromide even more readily than ethyl alcohol, also with less decomposition than it does the higher perbromide. It is slightly soluble in ethyl acetate, insoluble in chloroform and ether. It remains tolerably permanent when heated to  $100^\circ$  C., but, on prolonged heating, or at higher temperature, it is rapidly converted into bromocaffeine.

*Caffeine Hydrochloride Tetrabromide*,  $C_8H_{10}N_4O_6 \cdot HCl \cdot Br_4$ .—The preparation of this perbromide requires many precautions, for otherwise the product is impure, being mixed with the perbromide of the hydrobromide. First of all, the bromine must be perfectly free from hydrobromic acid, and the chloroform must be free from alcohol and moisture. Second, a dilute solu-

tion of bromine must be employed, so dilute that the addition of it to caffeine should produce no precipitation of the perbromide of caffeine hydrobromide within at least one-half hour. When all these conditions are observed, the perbromide of the hydrochloride is readily obtained by passing a stream of dry hydrochloric acid gas into a dilute solution of caffeine and bromine in chloroform. It separates in compact red crystals. The acid must be passed into the solution very slowly to prevent the formation of pure caffeine hydrochloride; care must also be taken to replace the bromine as it is gradually being used up, avoiding, however, a large excess of it at any time. The substitution of carbon tetrachloride for chloroform will not answer, for although caffeine is so readily soluble in the latter, it is almost insoluble in the former. Samples were washed with chloroform, dried in the usual manner, and analyzed for the exterior bromine and for hydrochloric acid. The latter was estimated by subtracting from the total weight of the mixed silver halides the quantity of silver bromide corresponding to the bromine as found by titration with sodium thiosulphate. The analysis furnished the following figures:

	Calculated for $C_8H_{10}N_4O_9.HCl.Br_4$ .	I.	Found. II.	III.
Bromine .....	58.14	56.75	56.70	56.00
HCl.....	6.61	6.98	....	....

This compound is of a somewhat lighter color than the corresponding hydrobromide. The crystals, when examined under the microscope, present the appearance of the distinct prisms. The perbromide melts at  $149^{\circ}$  C. sharp. Suspended in water, it remains unchanged for a time, then decomposes, and finally yields bromocaffeine. Methyl and ethyl alcohol, as well as ether, convert it into caffeine hydrobromide dibromide. Exposed to air, it loses bromine more rapidly than the corresponding tetrabromide of the hydrobromide. On gentle warming for two or three days it still retains a decidedly yellow color.

#### IV. PERHALIDES OF CHLOROCAFFEINE.

It appears from the results which have been presented that caffeine, although a weak base, forms tolerably stable and rather high perhalides. I have next attempted to prepare perhalides



of chloro- and bromocaffeine, and compare these with those of caffeine itself. One would judge, *a priori*, that the introduction of such strong negative elements as chlorine and bromine into a weak base, would greatly weaken its tendency to form perhalides. And yet, experience shows that the halogen substitution derivatives of caffeine are still capable of forming definite salts, and that they also form even higher perhalides than caffeine itself.

*Chlorocaffeine Hydriodide*,  $C_8H_9ClN_4O_2.HI$ .—This salt can only be prepared in absence of water. Chlorocaffeine, prepared according to E. Fisher's<sup>1</sup> method, is dissolved in chloroform, and a stream of dry hydriodic acid gas is passed into the solution. The salt soon separates in the form of white heavy crystals. These are filtered, washed with chloroform, dried first by exposure and finally over solid potassium hydroxide. The acid was estimated by suspending a weighed quantity in water and titrating with a twentieth-normal solution of potassium hydroxide, using phenolphthalein as an indicator.

	Calculated for $C_8H_9ClN_4O_2.HI$ .	Found.
HI .....	35.82	35.69

The salt is decomposed at once by water and alcohol. It gives up its hydriodic acid when exposed to air, probably through absorption of moisture, for when kept over potassium hydroxide for twenty hours it still contains 35.45 per cent. of hydriodic acid.

*Chlorocaffeine Hydrobromide*,  $C_8H_9ClN_4O_2.HBr$ .—This salt is prepared similarly to the hydriodide. It is, however, less stable and loses its acid more readily. Analysis gives the following figures:

	Calculated for $C_8H_9ClN_4O_2.HBr$ .	Found.
HBr .....	26.18	26.80

Kept over potassium hydroxide for ten hours it showed only 24.80 per cent. of hydrobromic acid.

*Chlorocaffeine Hydrochloride*,  $C_8H_9ClN_4O_2.HCl$ .—This salt is still less stable than the hydrobromide. It is necessary to wash it with chloroform saturated with hydrochloric acid, and dry for analysis as rapidly as possible.

<sup>1</sup> *Ann. Chem.* (Liebig), 218, 262.

	Calculated for $C_8H_9ClN_4O_3.HCl$	Found.
HCl .....	13.75	12.92

Kept over potassium hydroxide for 6 hours it showed only 6.15 per cent. of hydrochloric acid.

*Chlorocaffeine Hydriodide Pentiodide*,  $C_8H_9ClN_4O_3.HI.I_3$ .—Chlorocaffeine is dissolved in chloroform and is mixed with a solution of iodine in the same solvent. A slow stream of dry hydriodic acid gas is now passed into the mixture. A black amorphous powder separates at once. This is finely powdered and redigested with a fresh solution of iodine in order to insure complete reaction. If it had been previously completed, no further absorption of iodine will take place. The periodide is filtered, washed with chloroform, and dried in the usual manner. The "periodine" is estimated by titration with sodium thiosulphate. The total iodine is estimated by subtracting from the mixed silver halides (by Carius' method) the quantity of silver chloride which corresponds to the chlorine in the chlorocaffeine. The results of analysis are as follows :

	Calculated for $C_8H_9ClN_4O_3.HI.I_3$	I.	Found. II.	III.
Total iodine.....	76.78	76.15	....	....
Periodine .....	63.99	63.08	62.66	62.75

This periodide is a black amorphous powder with a slightly bluish tint. It melts at  $185^{\circ}$ – $6^{\circ}$  C. It is decomposed by water, alcohol, more readily by methyl alcohol, by ether and ethyl acetate, giving in all cases the white chlorocaffeine. It is slightly soluble in chloroform. Washing the periodide with a large amount of chloroform does not diminish the per cent. of the halogen in the compound. When exposed to air it shows only slight signs of alteration, and even on heating the periodide at  $100^{\circ}$  C. for twenty-four hours, only a portion of the iodine can be driven off.

*Chlorocaffeine Hydrobromide Pentiodide*,  $C_8H_9ClN_4O_3.HBr.I_3$ .—This periodide is prepared by the same method as the periodide just described, substituting hydrobromic for hydriodic acid. If the acid be passed rapidly, the periodide comes down amorphous; if slowly, it assumes a crystalline appearance. Redigestion in a fresh solution of iodine shows no increase in the per cent. of

iodine in the periodide. On being washed with pure chloroform the periodide suffers no appreciable loss of the halogen. It was analyzed with the following results :

	Calculated for $C_8H_9ClN_4O_3.HBr.I_4$ .		Found.	
	I.		II.	III.
Iodine .....	67.15	65.5	67.07	66.29
HBr.....	8.49	....	8.21	....

The hydrobromic acid was estimated by subtracting from the mixed silver halides (by Carius' method) the quantities of silver chloride and iodide which correspond to the chlorine of chlorocaffeine, and to the iodine as found by titration respectively.

In appearance this periodide is not quite as black as the periodide of the hydriodide. It melts at  $169^{\circ}$  C. It is however far less stable than the hydriodide, giving up its iodine very readily to water, alcohol, ether and ethyl acetate; somewhat soluble in chloroform. When exposed to air it loses its iodine very rapidly, and on gentle warming leaves pure chlorocaffeine. It is even more unstable than the periodide of the hydrochloride of chlorocaffeine, an irregular gradation of stability as compared with that of the periodides of caffeine itself.

*Chlorocaffeine Hydrochloride Tetraiodide*,  $C_8H_9ClN_4O_3.HCl.I_4$ . —The preparation of this compound has been attended with some difficulties, because of its greater solubility in chloroform than the other periodides. The results of analysis by themselves would not entirely justify the formula of the compound as given, had it not been supported by the analysis of the far more stable periodide of bromocaffeine hydrochloride, which certainly has the analogous constitution. Washed with chloroform and dried this periodide furnished upon analysis these figures:

	Calculated for $C_8H_9ClN_4O_3.HCl.I_4$ .		Found.	
	I.		II.	III.
Iodine .....	70.49	72.70	70.28	73.51 (?)

This periodide is of a blue-black color, and is crystalline. It melts at  $137^{\circ}$  C. It is decomposed by the different reagents similarly to the other periodides. It is however more stable than the periodide of the hydrobromide, losing iodine only very slowly on exposure to air. When gently heated it takes several hours to drive off all the iodine from a small sample of the periodide.

*Chlorocaffeine Hydrobromide Pentabromide*,  $C_8H_7ClN_4O_3.HBr.Br_5$ .—When a solution of chlorocaffeine in chloroform is treated with bromine and set aside, there appear within twenty-four hours long beautiful red crystals. The more bromine added, the quicker and more abundant is the crop; if quite a strong solution of bromine in chloroform be employed, the crystals appear within ten to fifteen minutes. On the other hand, the more carefully the bromine and chloroform are freed from traces of moisture, alcohol, and hydrobromic acid, the longer is the formation of the crystals delayed. But even with the most carefully purified reagents I have never failed to obtain them sooner or later. Several samples prepared independently were filtered, washed with chloroform containing some bromine, and rapidly dried. The total bromine was estimated by Carius' method. The analysis gave the following results:

	Calculated for $C_8H_7ClN_4O_3.HBr.Br_5$ .		Found.		
	I.	II.	III.	IV.	
Total bromine.....	67.66	65.98	....	66.57	....
Perbromine.....	56.38	55.25	55.02	55.42	55.00

The results of analysis show conclusively that we have here a perbromide of a hydrobromide. To confirm this, I have prepared the same compound by passing hydrobromic acid gas into a solution of chlorocaffeine and bromine in chloroform. The perbromide, which separated as a heavy amorphous sediment, gave these figures:

Total bromine.....	67.04
Perbromine .....	55.87

Whence comes the hydrobromic acid? Some of it at least is probably produced by the action of bromine upon traces of moisture present in the reagents. It is not improbable that some hydrobromic acid results from the substituting action of bromine upon chloroform, a reaction which is extremely slow when the reagents are pure, but may be induced or facilitated by the presence of foreign bodies, like chlorocaffeine in this case. Then again, a small portion of chlorocaffeine is probably decomposed, in some way, by bromine with the production of hydrobromic acid; and this, as soon as formed, unites with the unattacked chlorocaffeine and forms the perbromide. This would

explain why, even when pure reagents are employed, the formation of crystals begins very soon after the addition of bromine, provided it be added in large excess.

The perbromide, when crystalline, consists of dark-red short thick prisms. It melts at  $151^{\circ}$  C. It is decomposed by water, alcohol, ethyl acetate, giving a residue of pure chlorocaffeine. It is insoluble in chloroform. Ether removes only four-fifths of the "exterior" bromide, and gives a lower perbromide. Exposed to air it loses bromine quite readily, and if the exposure be prolonged, it loses all its bromine. Gentle heating greatly hastens the liberation of bromine.

*Chlorocaffeine Hydrobromide Monobromide*,  $C_8H_7ClN_4O_3 \cdot HBr$ . Br.—When the pentabromide of chlorocaffeine, finely powdered, is digested with anhydrous ether for several days, it gives up four-fifths of its "exterior" bromine. The reaction is slow towards the end and care must be taken to replace the ether with fresh portions of the solvent. The yellow residue is filtered off, washed with ether and rapidly dried. Several samples were analyzed with the following results :

	Calculated for $C_8H_7ClN_4O_3 \cdot HBr \cdot Br$ .		Found.	
	I.		II.	III.
Total bromine.....	41.08	42.34	....	....
Perbromine.....	20.54	22.11	20.89	20.04

It is a yellow amorphous powder, of a darker shade than the corresponding derivative of bromocaffeine. It melts at  $189^{\circ}$  C., being previously decomposed into chlorocaffeine and bromine. It resembles the pentabromide in most of its properties, but seems to be somewhat more stable toward methyl and ethyl alcohol.

*Chlorocaffeine Hydrochloride Pentabromide*,  $C_8H_7ClN_4O_3 \cdot HCl$ . Br.—Chlorocaffeine is dissolved in dry chloroform containing bromine free from hydrobromic acid. A slow stream of dry hydrochloric acid gas is now passed into the solution. Beautiful well defined crystals soon separate. These are filtered, washed with chloroform containing bromine, and rapidly dried. Several samples gave the following results upon analysis :

	Calculated for $C_8H_7ClN_4O_3 \cdot HCl \cdot Br_5$ .		Found.	
	I.		II.	III.
Br .....	60.17	58.88	57.62	58.50
HCl.....	5.48	5.61	....	....

The crystals, small prisms, are of a red to a scarlet-red color. The perbromide melts at  $153^{\circ}\text{C}$ . It is decomposed by water, alcohol and ethyl acetate in about the same degree as the perbromide of the hydrobromide. On exposure to air, or on gentle heating, it does not seem to lose bromine any faster than the perbromide of the chlorocaffeine hydrobromide.

#### V. PERHALIDES OF BROMOCAFFEINE.

Bromocaffeine, like the chloro compound, is capable of forming salts and perhalides, provided the proper conditions are observed. In general, the salts are even more stable than those obtained from chlorocaffeine; this is also true, in general terms, of the perhalides.

*Bromocaffeine<sup>1</sup> Hydriodide*,  $\text{C}_8\text{H}_7\text{BrN}_4\text{O}_9\cdot\text{HI}$ .—Prepared and analyzed like the corresponding salt of chlorocaffeine, it furnished these figures:

	Calculated for $\text{C}_8\text{H}_7\text{BrN}_4\text{O}_9\cdot\text{HI}$ .	I.	Found. II.	III.
HI.....	31.83	31.49	32.18	32.52

Kept over potassium hydroxide for two days it showed no loss of hydriodic acid.

*Bromocaffeine Hydrobromide*,  $\text{C}_8\text{H}_7\text{BrN}_4\text{O}_9\cdot\text{HBr}$ .—This salt has to be washed with chloroform saturated with hydrobromic acid, for otherwise it dissociates and gives upon analysis low results:

	Calculated for $\text{C}_8\text{H}_7\text{BrN}_4\text{O}_9\cdot\text{HBr}$ .	I.	Found. II.	III.
HBr.....	22.89	21.22	19.00	23.50

The salt is tolerably stable when protected from moisture.

*Bromocaffeine Hydrochloride*,  $\text{C}_8\text{H}_7\text{BrN}_4\text{O}_9\cdot\text{HCl}$ .—Prepared in the same manner as the other salts, it furnished the following results:

	Calculated for $\text{C}_8\text{H}_7\text{BrN}_4\text{O}_9\cdot\text{HCl}$ .	I.	Found. II.
HCl.....	11.77	11.79	11.43

This salt is far more stable than the hydrochloride of chlorocaffeine. Left over potassium hydroxide for twenty hours, it lost only 0.70 per cent. of hydrochloric acid.

*Bromocaffeine Hydriodide Pentiodide*,  $\text{C}_8\text{H}_7\text{BrN}_4\text{O}_9\cdot\text{HI}\cdot\text{I}_2$ .—This periodide has been prepared similarly to the analogous

<sup>1</sup> Prepared according to R. Fisher's method, *Ann. Chem.* (Liebig), 215, 264.

periodide of chlorocaffeine. Washed with chloroform, dried and analyzed, it gave the following results, as obtained upon separate samples :

	Calculated for $C_8H_8BrN_4O_2.HI.I_2$	I.	Found. II.	III.
Total iodine.....	73.42	72.86	....	....
Periodine .....	61.22	60.52	60.22	61.27

It is a dull-black amorphous powder, melting at  $183^\circ$  C. It is decomposed by water, alcohol, ether and ethyl acetate, but slower than the analogous periodide of chlorocaffeine. It is insoluble in chloroform. The sample that furnished analysis I. was boiled for some time with chloroform, and still gave upon titration with sodium thiosulphate 60.39 per cent. of iodine. It loses iodine very slowly on exposure, and even on warming the liberation of iodine is slow.

*Bromocaffeine Hydrobromide Pentiodide*,  $C_8H_8BrN_4O_2.HBr.I_5$ .—This periodide forms very slowly, and the product, as first obtained, must be redigested in fresh solutions of iodine in chloroform, in order to insure a uniform and constant sample. When all the salt has been thus converted into the pentiodide, further digestion with iodine does not give any higher periodide ; and when the pentiodide is washed with large quantities of pure chloroform, it loses none of its "exterior" iodine. Several samples were analyzed with the following results :

	Calculated for $C_8H_8BrN_4O_2.HBr.I_5$	I.	Found. II.	III.
I.....	64.12	65.40	63.88	64.53
HBr .....	8.12	....	8.42	....

This periodide is amorphous, of a dark-brown color, and melts at  $160^\circ$  C. It is decomposed by the different reagents like the similar periodide of chlorocaffeine. Unlike the latter, it loses iodine only very slowly on exposure, but quite rapidly when warmed. In this respect, then, it is a more stable compound than its analogue of chlorocaffeine.

*Bromocaffeine Hydrochloride Tetraiodide*,  $C_8H_8BrN_4O_2.HCl.I_4$ .—Just as the hydrochloride salt of bromocaffeine is more stable than the hydrochloride of chlorocaffeine, so is the periodide of the former easier obtained in pure state than that of the latter. When hydrochloric acid gas is passed into a solution of bromo-

caffeine and iodine in chloroform, the periodide comes down at once pure, either in brown or dark-blue crystals, depending upon the rate with which the hydrochloric acid is passed into the solution. Samples were washed with chloroform containing hydrochloric acid, dried and analyzed with the following results:

	Calculated for $C_8H_8HBrN_4O_2.HCl.I_2$	I.	Found. II.	III.
I.....	62.06	61.50	60.53	61.14
HCl.....	4.46	4.27	....	....

Bromocaffeine, then, agrees with chlorocaffeine in that respect that they both form *tetraiodides* of their respective hydrochlorides. The periodide of bromocaffeine hydrochloride is much less stable than the periodide of the hydrobromide, and in this respect bromocaffeine differs from chlorocaffeine, for in the latter the gradation of the stability is in the reverse order. This periodide consists of well defined brown or dark-blue crystals, melting at  $136^\circ$  C. It is readily decomposed by the various reagents. Exposed to air, it loses nearly all its iodine in a comparatively short time, and still more rapidly when warmed.

*Bromocaffeine Hydrobromide Pentabromide*,  $C_8H_8BrN_4O_2.HBr.Br_2$ .—All that has been said about the formation of the perbromide of chlorocaffeine applies equally well in the case of bromocaffeine. A solution of the latter in chloroform containing bromine begins to deposit long slender crystals within five to six hours, and the crop gradually increases as the solution is allowed to stand. Even when the reagents employed are carefully freed from traces of moisture and hydrobromic acid, the formation of the perbromide still takes place, being more rapid as the amount of bromine added is increased. The perbromide, thus obtained, is entirely identical with the one which is formed when dry hydrobromic acid gas is passed into a solution of bromocaffeine and bromine in chloroform, except that in the latter case the product is amorphous. All that has been said about the possible sources of the hydrobromic acid in the case of the perbromide of chlorocaffeine, must apply fully as well to the perbromide of bromocaffeine. Unfortunately, neither of the two halogen substitution products of caffeine are soluble in carbon tetrachloride, and therefore the latter could not be used instead of



chloroform. The total bromine was found by subtracting from the total silver bromide, as obtained by Carius' method, that amount of it which corresponds to the bromine in bromocaffeine proper. The results of the analysis of several samples are as follows :

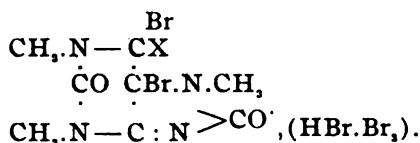
	Calculated for $C_8H_8BrN_4O_2 \cdot HBr \cdot Br_2$	I.	II.	Found. III.	IV.	V.
Total bromine.....	63.68	64.17	....	64.31	....	64.53
Perbromine .....	53.05	54.15	53.23	53.40	53.25	53.65

Analyses I., II., III. and IV. are upon samples prepared without the addition of hydrobromic acid, while Analysis V. is upon a sample obtained with addition of the acid.

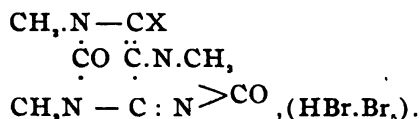
This perbromide consists of short prisms of a dark orange-red color, melting at  $156^\circ$  C. It resembles in general behavior the analogous perbromide of chlorocaffeine. It is decomposed by the various reagents, and on exposure loses all its bromine. When treated with ether it, too, forms the lower perbromide.

It may be said, that whatever the case be with pure caffeine itself, the perbromides of the halogen substitution derivatives of the base may after all have two bromine atoms linked to the unsaturated carbon atoms, and only the three remaining bromine atoms form the true perbromide. That is, the constitution of the perbromides should be represented by Formula I, and not by II.

I.



II.



In favor of this view, we have the fact that the introduction of a negative group (X) into the caffeine molecule favors the formation of such additive products. Thus, E. Fisher<sup>1</sup> has found

<sup>1</sup> *Ann. Chem.* (Liebig), 215, 272.

that hydroxycaffeine readily unites with bromine, and the resulting additive product has not unlikely this composition:  $C_8H_9(OH)N_4O_5.Br_2$ . But against this view we have (1) that no such dibromo-additive compounds of either chloro or bromocaffeine have ever been isolated; (2) that even iodine makes the penta-perhalides, and not the tri-perhalides, as we should otherwise expect, and (3) that the formation of the perhalides of bromo and chlorocaffeine takes place only in presence of some halogen acid.

*Bromocaffeine Hydrobromide Monobromide*,  $C_8H_9BrN_4O_5.HBr.Br$ .—This is formed when the higher perbromide is treated with anhydrous ether until fresh portions of the latter are no longer colored by the perbromine. Washed with ether and dried, several independent samples were analyzed with the following results:

	Calculated for $C_8H_9BrN_4O_5.HBr.Br$ .		Found.	
	I.		II.	III.
Total bromine.....	36.86	37.35	....	....
Perbromine .....	18.43	18.68	20.39	20.04

This perbromide is of a lighter yellow color than the corresponding perbromide of chlorocaffeine; in all other respects the two compounds apparently agree. It melts at  $206^\circ C.$ , suffering, previously to melting, decomposition into bromocaffeine, hydrobromic acid, and bromine.

*Bromocaffeine Hydrochloride Pentabromide*,  $C_8H_9BrN_4O_5.HCl.Br_5$ .—Bromocaffeine is dissolved in chloroform, bromine free from hydrobromic acid is added, and a slow stream of hydrochloric acid gas is now passed into the mixture. The separation of the perbromide begins to take place at once, in the form of deep-red needle-like crystals. Samples thus prepared were analyzed with the following results:

	Calculated for $C_8H_9BrN_4O_5.HCl.Br_5$ .	I.	Found.	II.
Br .....	56.40	55.25		55.18
HCl .....	5.13	5.02		....

This perbromide resembles very closely the perbromide of the hydrobromide, but it seems to give off bromine more readily than the latter. It melts at  $157^\circ C.$  It is decomposed by the various reagents, and gives pure bromocaffeine.

## VI. SUMMARY.

The results described in the preceding pages are presented in a condensed form in the subjoined table. In general terms, the perhalides, as given in the table, decrease in stability as we read from left to right. For example, of the periodides of the hydriodides, that of caffeine is the most stable, next comes that of bromocaffeine, and this is followed by the one of chlorocaffeine. The same is true of the periodides and perbromides of the other salts. While the line is quite sharp between the perhalides of caffeine and those of bromocaffeine, it is not so between the perhalides of the latter and those of chlorocaffeine. We can speak only in general terms of a difference in stability between the perhalides of the two halogen caffeines, respectively. Thus, we notice such a difference in stability between the periodides of the two hydrobromides, and also between the perbromides of the two hydrochlorides respectively. The gradation in stability among the periodides of one and the same class is usually, but not always, regular. In all three cases, however, the periodides of the hydriodides are far more stable than those of the other salts. If *a*, *b*, and *c* should represent different degrees of stability, decreasing in alphabetical order, then the *relative* stability of the members of each class of the perhalides is as is given in the table. It must be understood that the term *stability* is used here in its broad and general sense, such as the behavior of the compounds towards different solvents, and on exposure to air. The comparison is made between the perhalides of each class, and the periodides, as well as the perbromides of each of the three bases (caffeine, bromocaffeine, and chlorocaffeine) form separate classes for comparison. When two perhalides of the same salt exist, only the higher one is taken into account.

There appears to be a regular lowering in the melting points of the periodides of each class, it being the highest in the hydriodides and the lowest in the hydrochlorides. It is a curious coincidence that the melting points of the analogous periodides of chlorocaffeine and bromocaffeine are so near alike, while the pure halogen caffeines themselves melt at 188° C. and 206° C., respectively. The perbromides do not show such a regular gradation. There is a difference in stability of the periodides of each class, corresponding to the lowering of the

CAFFEINE.			BROMOCAFFEINE.			CHLOROCAFFEINE.		
Acid com- bined with base.	Perhalides.	Sta- bility.	M. P.	Perhalide.	Sta- bility.	M. P.	Perhalide.	Sta- bility.
Periodides.	HI. $C_8H_{10}N_4O_7 \cdot HI \cdot I_2$		171°					
	HI. $C_8H_{10}N_4O_7 \cdot HI \cdot I_4$	<i>a</i>	215°	$C_8H_7BrN_4O_7 \cdot HI \cdot I_4$	<i>a</i>	183°	$C_8H_9ClN_4O_7 \cdot HI \cdot I_2$	<i>a</i>
	HBr. $C_8H_{10}N_4O_7 \cdot HBr \cdot I_4$	<i>b</i>	183°	$C_8H_7BrN_4O_7 \cdot HBr \cdot I_2$	<i>b</i>	160°	$C_8H_9ClN_4O_7 \cdot HBr \cdot I_2$	<i>c</i>
	HCl. $C_8H_{10}N_4O_7 \cdot HCl \cdot I_2$	<i>c</i>	165°	$C_8H_7BrN_4O_7 \cdot HCl \cdot I_4$	<i>c</i>	133°	$C_8H_9ClN_4O_7 \cdot HCl \cdot I_4$	<i>b</i>
Perbromides.	HBr. $C_8H_{10}N_4O_7 \cdot HBr \cdot Br_2$		170°	$C_8H_7BrN_4O_7 \cdot HBr \cdot Br$		206°	$C_8H_9ClN_4O_7 \cdot HBr \cdot Br$	189°
	HBr. $C_8H_{10}N_4O_7 \cdot HBr \cdot Br_4$	<i>a</i>	170°	$C_8H_7BrN_4O_7 \cdot HBr \cdot Br_2$	<i>a</i>	156°	$C_8H_9ClN_4O_7 \cdot HBr \cdot Br_2$	<i>a</i>
	HCl. $C_8H_{10}N_4O_7 \cdot HCl \cdot Br_4$	<i>b</i>	149°	$C_8H_7BrN_4O_7 \cdot HCl \cdot Br_2$	<i>b</i>	157°	$C_8H_9ClN_4O_7 \cdot HCl \cdot Br_2$	<i>b</i>

melting points, this being true of caffeine and bromocaffeine, where the periodide of the hydrobromide is less stable than the hydrochloride. There is a uniformity in composition between the periodides on one hand and the corresponding perbromides on the other, in each of the three bases. Thus, in caffeine it is always the tetrahalide compound that is more easily formed, and in chlorocaffeine and bromocaffeine it is the pentahalide. It will be noticed that all three hydrochlorides carry less iodine in the periodides than the salts of the other two halogen acids.

It is difficult to draw very general conclusions from the study of perhalides of only one base, but so far as they go, the results presented in the preceding pages justify in a certain degree the following conclusions :

(1) Organic bases are capable of forming periodides not only of their hydriodide salts, but also of the hydrobromides and of the hydrochlorides. The stability of the resulting periodide will be governed, all other conditions being equal, by the nature of the halogen through which the "periodine" is linked to the nitrogen, decreasing as the volatility of the halogen increases.

(2) When a base forms periodides, it is also capable of forming perbromides, which probably possesses an analogous composition and constitution.

(3) If two nearly related compounds form under similar conditions periodides (or perbromides) of different degrees, then the periodide (or perbromide) containing the highest number of "perhalogen" atoms is not necessarily the more stable of the two. Compare, for instance, the tetraiodide and tetrabromide of caffeine with the pentiodide and pentabromide of bromocaffeine.

(4) The number of iodine atoms which a base takes up in the formation of a periodide is in no way an index of the basal power of the base. Caffeine, for instance, is a very weak base, yet it forms higher periodides than the comparatively stronger bases of morphine, strychnine, atropine, etc. Again, chlorocaffeine and bromocaffeine, although far weaker than caffeine itself, forms higher periodides than the latter.

In conclusion, I wish to express my thanks to Mr. J. A. Keating and Mr. W. J. O'Brien, who have kindly helped me in this work.

ANN ARBOR, MICHIGAN.

## DETERMINATION OF THE HEAT OF BROMINATION IN OILS.<sup>1</sup>

BY H. W. WILEY.

Received January 3, 1896.

THE qualitative value of the degree of heat produced in mixing oils with sulphuric acid, is pointed out in Bulletin No. 13, Part IV, pages 475 *et seq.* In that bulletin a great number of examples are given, showing the different behavior of different fats and oils when treated according to the method first proposed by Maumené with sulphuric acid under standard conditions. It is evident that in a process of this kind the actual rise of temperature observed is dependent upon many varying conditions, such as the initial temperature, strength of sulphuric acid, relative proportions of sulphuric acid and oil employed, perfectness of insulation and other data depending on the analytical system itself. The data obtained under standard conditions, however, are extremely valuable in discriminating between fats of different characters. For instance, the rise of temperature produced by a given weight of butter fat is only about one-fourth of that produced by an equal weight of cotton oil under the same conditions. In the bulletin mentioned above, formulas are also given whereby some quantitative idea may be obtained of the relative proportions of the two constituents in a mixed oil. The fact that the natural glycerides contain unsaturated radicals capable of combining with the halogens has long been recognized, and Hübl, as is well known, has based a quantitative method of great value upon the ability of glycerides to absorb iodine. Chlorine and bromine are also absorbed with equal or greater avidity, and attempts have been made to establish quantitative methods in which these halogens take the place of iodine in the Hübl process.

Hehner and Mitchell<sup>2</sup> propose an innovation upon the general principles of the Hübl method in which the degree of chemical action is not measured by the residue of the halogen left unabsorbed, but by the degree of heat produced by the chemical reaction which takes place. They have not made any attempt

<sup>1</sup> Read at the Cleveland Meeting, December 31, 1895.

<sup>2</sup> Analyst, 20, 146.

to determine the total quantity of heat by calorimetric measurement, but simply estimate the total rise of temperature produced by the reaction. This method I have subjected to a thorough analytical test, and am convinced that it has great value in



analytical operations. On account of the difficulty of executing the method as described by the authors, I have made a number of changes therein which render it not only more accurate, but, especially, more easy of application. The difficulty of handling liquid bromine in quantities of one cc. is evident to every

analyst. It is almost impossible to measure and deliver exactly this quantity of liquid bromine into the tube in which the reaction takes place. I have therefore made use of the bromine previously dissolved in chloroform or carbon tetrachloride. I find that one part by volume of bromine in four parts by volume of chloroform makes a solution which is easily kept and easily measured. To avoid any disturbing action of the bromine upon the chloroform, due to the generation of hydrobromic acid, the solution should be kept shielded from the light and only small quantities, such as may be used during the day, made up at a time. Another convenient modification has been introduced in dissolving the fats or oils in chloroform or carbon tetrachloride before beginning the analytical operations. By this means triplicate determinations, or a greater number may be made on the same sample without the trouble and annoyance of weighing each one. Ten grams of the oil or fat are dissolved in chloroform and the volume made up to fifty cc. With this volume nine determinations can easily be made, and it is recommended that at least four be made with every sample.

The apparatus employed is shown in the illustration. The tube holding the reagent and thermometer is about forty centimeters in length and one and a half in internal diameter. It is conveniently held in a drying jar, into which it fits air-tight by means of a rubber stopper. In order to secure the insulation of the inner tube, the air is withdrawn from the drying cylinder through the side tubulure. The solution of bromine and chloroform is placed in a heavy Erlenmeyer flask with a side tubulure near the top, to which is attached a rubber bulb. The flask carries a pipette held in place by a stopper, which by gentle pressure is made air-tight. The thermometer used is graduated in fifths of degrees and it is easily read to tenths by means of a small magnifying glass.

The operation should be conducted in a room which is kept at as nearly as possible constant temperature during the progress of the work.

The solutions having all been prepared, they are placed upon the table with the apparatus and the whole system is allowed to stand until a constant temperature through all parts is reached.



Five cc. of the solution of the fat or oil are placed in the inner tube by means of a pipette, with care to prevent the solution coming in contact with the walls of the tube. The thermometer having been inserted, the bromine solution is forced into the pipette by compressing the rubber bulb with the left hand until the liquid has passed the mark on the stem of the pipette. The top of the pipette is now closed by the forefinger of the right hand, the pressure on the rubber bulb released, the stopper in the Erlenmeyer flask loosened and the bromine in the pipette allowed to flow out until the mark is reached. The bromine solution is transferred to the observation tube and allowed to flow directly into the solution of the fat. It is not important, in this case, to prevent the liquid from touching the sides of the tube as it enters. As soon as the pipette is empty it is withdrawn, replaced in the Erlenmeyer flask and the thermometer at once observed by means of the magnifying glass. The bromination of the fat is practically instantaneous and the mercury in the thermometer will reach its maximum height in about a minute after the pipette delivering the bromine solution is withdrawn. The whole operation of determining the heat of bromination after all the preparations are made can be accomplished within two minutes. When the mercurial column in the thermometer begins to descend, air is admitted into the outer cylinder through the stopcock shown, the tube containing the residue of the reaction is withdrawn by loosening the rubber stopper and its contents emptied. By holding the tube with the mouth down the residual bromine vapor soon escapes and the tube may be cleaned by simply wiping it with a long test-tube cleaner, or may be used again without cleaning after allowing it to stand for half an hour mouth down. Any traces of brominated oil which remain upon the sides of the tube do not unfit it for subsequent use, unless thick enough to obscure the reading of the temperature. By allowing the air thus to re-enter the jacket space the thermometer is soon restored to the normal, and a second determination may be made within half an hour. In this way two determinations an hour can be made with the same system.

In regard to the relation which the rise of temperature, due to

bromination, has to the iodine absorption number of a fat, it is stated by Hehner and Mitchell that it is represented by the factor 5.5. It is evident, however, that this factor must be determined separately for every system of apparatus and every solvent employed. Naturally it would be different from the number stated when determined in the manner indicated above. Each analytical system, therefore, must be separately standardized, and the factor thus obtained can be used with considerable certainty for calculating the number representing the iodine absorption.

It may be mentioned that it is important not to stir or churn the mixture of the oil and bromine further than is secured by the introduction of the bromine solution itself. By a vigorous churning of the mixture, throwing the warm liquid against the cold sides of the containing tube, I found it possible to reduce the rise of temperature in one instance from  $19^{\circ}$  to less than  $15^{\circ}$ . It is evident that much more accurate results could be obtained in all cases by a careful calorimetric measurement of the heat produced by the reaction. For strictly scientific purposes, this is the only rational method of procedure, but the desired end will be served equally well by carefully conducting the process in some such way as indicated above and determining for each system of apparatus employed the factor for calculating the iodine number.

Experience has shown that carbon tetrachloride, by reason of its higher boiling-point and stability, is a more convenient solvent in the preparation of the reagents than chloroform. The rise of temperature obtained, however, with solutions in carbon tetrachloride, is slightly less than in chloroform. This is not due to a higher specific heat of the carbon tetrachloride, since at  $30^{\circ}$  the specific heats of the solvents are 0.207 and 0.233 for carbon tetrachloride and chloroform respectively. Either the action of the bromine is more vigorous in the chloroform solution or else the heat due to the bromination of the chloroform and the production of hydrobromic acid is sufficient to account for the difference. In other words, we have here to deal not only with the heat of bromination of the oil, but also with that due to the formation of  $\text{CBrCl}_3$  and of hydrobromic acid. This is an addi-

tional reason for preferring carbon tetrachloride as a solvent.

This action is indicated by the following data: One part of bromine and four of chloroform were placed in separate contiguous vessels, in a room subject only to slow changes of temperature, and left at rest for nineteen hours. The temperature of the two liquids at the expiration of this time was exactly  $12^{\circ}$ . On placing the thermometer in the bromine and pouring the chloroform upon it there was at first a depression of the temperature amounting to seven-tenths of a degree. In a few seconds the temperature began to rise, and at the end of three minutes it had reached  $13.3^{\circ}$ , showing a rise of over one degree above that of the original solutions.

In the following table the data representing the means of several observations in each instance are given, showing the results of the determination of the heat of bromination of four oils dissolved in the one instance in chloroform and in the other in carbon tetrachloride:

Name of oil.	Solvents.	Initial temperature.	Final temperature.	Rise of temperature.
Olive oil	Chloroform	$22.7^{\circ}$	$42.2^{\circ}$	$19.5^{\circ}$
Olive oil	Carbon tetrachloride	15.1	33.3	18.2
Calycanthus seed oil	Chloroform	17.2	45.9	28.7
Calycanthus seed oil	Carbon tetrachloride	19.3	47.0	27.7
Salad oil (cotton seed?)	Chloroform	17.9	43.7	25.8
Salad oil (cotton seed?)	Carbon tetrachloride	19.8	44.7	24.9
Sunflower seed oil	Chloroform	15.0	43.4	28.4
Sunflower seed oil	Carbon tetrachloride	14.0	41.6	27.6

My thanks are due to Mr. E. E. Ewell for assistance in the analytical work.

#### DISCUSSION.

*Dr. C. B. Dudley:* The detection of adulterations in commercial oils is a subject that has given us an immense amount of study in the laboratory at Altoona. The commercial results may be easily imagined when it is known that at one time during the past eighteen years lard oil was worth \$1.10 a gallon, and cottonseed oil fifty cents a gallon, and that it was no uncommon practice to put into a gallon of lard oil as high as twenty-five per cent. of cottonseed oil. I should state that lard oil is used in making burning oil for hand lanterns and is commonly called signal oil. On this oil depends largely the safety of the running of

trains. Cottonseed oil being, as you all know, a semi-drying oil, and does not burn well, hence the seriousness of adulteration may be readily understood. Signal oil mixed with cottonseed oil will go out in from six to eight hours after it is lighted, at least after the first two or three times burning of a wick. The switches must be lighted fourteen hours continuously to insure safety, and the hand lanterns for signalling must be reliable. No small amount of the work done at Altoona has been done in connection with adulterations in oils. We have kept pace with every modification that would enable us to detect adulteration, and have found Maumene's test of very great value, because of its simplicity, its rapidity of application, and the constancy of the results obtained.

There are two serious defects, however, in all the tests that I have ever seen proposed for detecting adulterations in oils. These are: First, none of the proposed methods are based on any characteristic reactions of any given oil so that although we may be able to say that a sample of oil submitted to us is not pure, we are unable to say what other oil it is adulterated with. The second defect is that owing to this lack of characteristic reactions and to the peculiarities of the proposed method, mixtures of various oils can be made, which mixtures will give the same results under the tests as a pure sample of another oil. For example, it is quite easy to make such a mixture of olive and cottonseed oils that the rise in temperature obtained by Maumene's test will be the same as is characteristic of pure lard oil. And the same may be said of the iodine test, etc. So far as our knowledge goes we still lack a means of identifying the characteristic oil that may be present as an adulterant in another, and also we still lack an absolute means of saying positively that a sample of an oil is not a pure one.

## SÄRNSTRÖM'S METHOD OF DETERMINING MANGANESE IN IRON ORES.

BY C. T. MIXER AND H. W. DUBOIS.

Received February 25, 1896.

ABOUT a year ago we had occasion to use a volumetric method which would allow the determination of manganese in iron ores ranging in amounts up to fifteen per cent. and give results in half an hour which would check with gravimetric determinations within two-tenths per cent. for ores as high as fifteen per cent., and within a few hundredths of a per cent. for ores under one per cent.

We found in use in a neighboring laboratory a method which was generally known as the "Swedish Method." This method was found to fulfill the above conditions, and seems to have sufficient merit to be more widely known.

The first suggestion upon which the method is based was made by Guyard,<sup>1</sup> although his method of operating it did not give very satisfactory results.

The first description of the method in its present practicable form, was made by C. G. Särnström, in the *Jernkontorets Annaler*, (Sweden), 1881, p. 401.<sup>2</sup>

The principle upon which this method depends, is the reaction which takes place when a manganese compound higher in oxygen than the manganous state, is dissolved in hydrochloric acid, forming a higher chloride, which is readily shown by the dark colored solution. When this solution is boiled, it rapidly decolorizes, being completely converted into manganous chloride, not easily oxidized by the air while in the acid solution.

In neutral or alkaline solutions the manganous compound has a slight tendency to oxidize in contact with the air, but we have never detected any appreciable oxidation under the conditions which we follow.

The separation of the iron and the manganese is effected in

<sup>1</sup> Guyard: *Chem News*, 8, 292; the following references relate to the subsequent modifications of the method; Habich: *Ztschr. anal. Chem.*, 3, 474; Winkler: *Ztschr. anal. Chem.*, 3, 423; Morawski und Stingl: *J. prakt. Chem.* (N. F.), 18, 96; Volhard: *Ann. Chem.* (Liebig), 198, 318.

<sup>2</sup> Also published in *Berg und Hüttenm. Zeitung*, 40, 425. A review of the original article appears in the *Ztschr. anal. Chem.*, 22, 84. We are indebted to Mr. Hugo Carlson, Chief Chemist of the Johnson Works of Lorain, Ohio, for calling our attention to Särnström's original publication and for furnishing us a translation of the same.

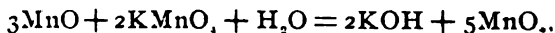
such a way that the iron is precipitated as hydroxide and the manganese left in the manganous condition in solution. Sodium carbonate is used to precipitate the iron as hydroxide and no trouble is experienced in the precipitation of the manganese as a carbonate, provided that only a very slight excess is employed beyond that necessary to completely precipitate the iron. It is advisable to add the sodium carbonate in the form of a solution, towards the completion of the precipitation of the iron, to avoid such an excess.

Särnström employs sodium bicarbonate, which has the advantage that a greater amount of carbon dioxide is generated, preventing subsequent oxidation of the manganous salt by the oxygen of the air. Manganese bicarbonate is formed, which is readily soluble in the solution containing carbon dioxide.

It is always desirable to test the sodium carbonate or bicarbonate for organic matter.

The results given below show the necessity of avoiding an excess of sodium carbonate (the same is true of the bicarbonate) in the precipitation of the iron. Aliquot portions of a solution of manganese containing 3.14 per cent. manganese gravimetrically determined, gave only 2.61 per cent. when treated with such an excess. Another ore giving 8.69 per cent. under the proper conditions of this method, when treated with an excess of sodium carbonate gave 5.38 per cent.

After the precipitation of the iron in the hot solution, the manganese being in the manganous state, is oxidized by potassium permanganate, according to the following formula,



which is the same reaction which takes place in Volhard's method. As the titration takes place directly, without filtering, the precipitate of ferric hydroxide is an advantage, especially in low manganese ores, as it serves to collect the fine precipitate of manganese dioxide and causes it to settle more rapidly.

In ores very low in iron, it is desirable to add ferric chloride in order to obtain the requisite amount of the iron precipitate.

*The Method.*—Weigh half a gram ore into a No. 6 beaker, add fifteen cc. of hydrochloric acid, 1.1 sp. gr., and boil until

the residue is clear. If necessary fuse the residue with sodium carbonate. Add a few drops of nitric acid to oxidize any ferrous iron or organic matter. In magnetic ores more of course will be necessary. It is well to test for ferrous iron. Evaporate a short time to expel any nitrous acid that may have been formed. It is advisable to have a good amount of free hydrochloric acid present to generate carbon dioxide in the precipitation with sodium carbonate. The solution is then washed into a No. 3 beaker or a flask, which is then filled about two-thirds full with boiling, distilled water and solid sodium carbonate or bicarbonate added until the iron is completely precipitated, which is readily indicated by the characteristic spongy appearance of the precipitated ferric hydroxide. A solution of the salt is preferable for the final precipitation in order to avoid an excess.

The solution should be about 80° C. when it is titrated<sup>1</sup> with potassium permanganate directly, without filtering, and with intervals of vigorous stirring and settling of the iron and manganese precipitates, until the supernatant liquid shows a permanent faint pink color. The first appearance of the pink color must not be taken as an indication that the oxidation is complete, as gentle heating and vigorous stirring will allow more potassium permanganate to be added before the permanent pink appears.<sup>2</sup>

Multiplying the burette reading by two represents the equivalent for one gram, and this multiplied by the permanganate value in manganese, which is the iron value multiplied by 0.2946, gives the percentage of manganese.

In case of overtitation, it is practicable to titrate back with a carefully standardized solution of manganous chloride, which is prepared by evaporating fifteen cc. potassium permanganate down to three or four cc., adding a few drops of hydrochloric acid and boiling as long as chlorine comes off. The solution should be neutralized with sodium carbonate and diluted to ten cc., when one cc. is equal to one cc. of potassium permanganate.

Särnström states that the method is reliable for high manga-

<sup>1</sup> Which should be done immediately after the neutralization, in order to avoid any opportunity for oxidation.

<sup>2</sup> This is a very important point not only in relation to this method, but in all methods where potassium permanganate is used.

nese ores and ferro-manganese "where it is not necessary to determine the manganese closer than a few tenths of one per cent."

Our experience does not confirm this. The results average from one to two per cent. too low, so that we do not consider the method at all reliable for high percentages of manganese.

The following are some results which show this :

	Särnström. Per cent.	Gravimetric (Ford's.) Per cent.
Illinois Ore .....	52.06 (1)	52.98
.....	51.91 (2)	....
.....	51.40 (3)	....
.....	51.78 (4)	....
.....	51.37 (5)	....
.....	51.37 (6)	....
No. 595.....	42.07	....
.....	42.35	44.3
.....	42.90	....
.....	42.60	....

In analyses from No. 1 to No. 4 sodium carbonate was used for the precipitation. To determine whether the employment of sodium bicarbonate would be advantageous, No. 6 was so treated while at the same time No. 5 was precipitated with sodium carbonate, yielding the same result. We have tried sodium bicarbonate with low manganese ores, but have never noticed any practical advantages, while theoretically, as we have pointed out above, there should be an advantage in the employment of sodium bicarbonate.

This discrepancy with high percentages of manganese may possibly be accounted for, by the fact that the large precipitate of manganese dioxide may act in a purely mechanical way in protecting the final amounts of the manganous chloride from being fully oxidized to dioxide by the potassium permanganate. It is to be noted in this connection that Volhard's method does not generally give reliable results with such high percentages of manganese.

The following are some results obtained by this and other methods :



	Särnström.	Volhard.	Gravimetric.
A. Magnetic .....	0.07	0.10	0.07
Specular .....	...	0.08 <sup>1</sup>	...
B. Mixture of blue } ..	0.30	0.31	0.29
granular and red } ..	0.32	0.29	0.30
hematite. } ..	0.28	...	...
C. Limonite .....	1.03	1.02	1.09
.....	1.05	1.05	...
D. Silicious ore.....	2.98	3.08	2.93
.....	3.07	3.07	...
Cary Empire.....	3.93	T. V. Church	{ 3.94
.....	3.88	Illinois Steel Co	
Dexter No. 2.....	{ 6.04	...	...
	{ 6.02	6.02	6.01
	{ 6.01	...	...
Davis ore .....	8.78	8.62	8.86
Newark ore.....	1.48	A. G. McKenna,	{ (Ford's)
	No. 57 .....	Duquesne Steel Works,	
	No. 218.....	5.39	
		5.59	...

In the determination of small amounts of manganese this method presents an advantage over Volhard's method in giving a more distinct end reaction.

The method can be used for iron and steel determinations if the usual precautions are taken to oxidize the carbon. But it is not so well adapted to these on account of the impracticability of taking large amounts for analysis.

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## ON VARIOUS MODIFICATIONS OF THE PEMBERTON VOLUMETRIC METHOD FOR DETERMINING PHOSPHORIC ACID IN COMMERCIAL FERTILIZERS.

By F. P. VEITCH.

Received February 18, 1896.

**I**F an excuse is needed for adding to the already voluminous literature on the method as proposed by Pemberton<sup>1</sup> and modified by Kilgore, it is found<sup>2</sup> in the action taken by the Association of Official Agricultural Chemists at their last meeting. The method, as modified by Kilgore, gave almost uniformly excellent results on known solutions, in a two years trial in the hands of a number of analysts, and only failed to become

<sup>1</sup> This was so low as to necessitate filtering through asbestos in order to see end reaction by Volhard's method.

<sup>2</sup> This Journal, 15, 382.

<sup>3</sup> Bul. 43, Div. Chem. U. S. Dept. Agr., 104.

an official method because many of the members had not worked with it.

During the past fall the writer has used the Kilgore modification as a check in quite a number of gravimetric determinations with very satisfactory results. While this modification may be considered as accurate as the molybdate for this class of work, at least on low percentages and in careful hands, it was felt that if the exact time and temperature elements could be gotten rid of, there would be a saving of both time and care where a large number of determinations were to be made. With this end in view, it was determined to study the following points :

1. The method of filtering and washing.
2. The time of standing after adding the molybdate solution.
3. The use of tartaric acid to prevent the precipitation of molybdic acid.

With regard to the first point it was found desirable to use simply the paper and funnel, doing away with the use of pressure and filtering twenty at a time. To simplify washing the dilute nitric acid and three per cent. potassium nitrate were omitted from the washings.

As the filter paper and funnel have been used with pressure with satisfactory results, there seems to be no objection to the use without pressure, so to condense the work as much as possible, the subjects were studied in pairs, as follows :

*A.* The method of filtering and washing and the time of standing after adding the molybdate solution.

*B.* The method of filtering and washing, and the use of tartaric acid to prevent the precipitation of molybdic acid.

***A.* THE EFFECTS OF THE METHOD OF FILTERING AND WASHING AND THE TIME OF STANDING AFTER ADDING THE MOLYBDIC SOLUTION.**

After some preliminary work, during which the volumetric method, as carried out at the New Jersey Station,<sup>1</sup> was tried and found to work very satisfactorily, it was determined to try the effect of standing for one half hour and for one hour at from 40°-50°C. It was thought best to allow some range of tempera-

<sup>1</sup> Bul. 43, Div. Chem. U. S. Dept. Agr., 92.

ture, as the care required to maintain a constant temperature is considerable.

The molybdate used was the official solution, to which ten cc. 1.42 sp. gr. nitric acid per cubic centimeter had been added. After standing the required length of time, the solutions were filtered off without pressure, the precipitates washed three times by decantation, allowing the precipitate to settle each time before decanting, the precipitates then transferred to the filters, the beakers washed out thoroughly and the precipitates washed until the wash water was neutral to litmus paper, which required from 200 cc. to 300 cc.; this latter amount has been found to free the precipitate from adhering acid in every instance. To feel sure that no appreciable amount of acid was retained in the filter, the washing was continued in a number of cases after no reaction was given with litmus paper, the washing received in clean beakers and titrated with the standard solutions. Table I gives the amount of acid removed by this extra washing as expressed in percentages of  $P_2O_5$ .

TABLE I.—THE AMOUNT OF ACIDITY EXPRESSED AS  $P_2O_5$  RETAINED IN PRECIPITATES AFTER WASHINGS WERE NEUTRAL TO LITMUS PAPER.

Number.	Amount of washing until cc. neutral to litmus paper.	Amount of washing after cc. neutral to litmus paper.	Amount of acidity in last wash water, expressed as $P_2O_5$ . Per cent.	Per cent. $P_2O_5$ in precipitate on filter. Per cent.	Remarks.
1	140	50	0.00	2.14	
2	135	"	0.01	2.81	
3	140	"	0.01	1.88	
4	200	"	0.04	1.48	Blue on filter hard to
5	150	"	0.00	2.52	free from
6	225	75	0.05	9.68	acid.
7	"	"	0.025	12.93	
8	"	"	0.025	6.46	
9	"	"	0.025	15.35	
10	"	"	0.000	15.28	
11	"	"	0.000	10.10	
12	"	"	0.000	17.09	
13	"	"	0.000	17.65	
14	"	"	0.025	22.10	
15	"	"	0.015	20.77	

Average..... 0.016 per cent.

(6)

These results show that when the washings become neutral to litmus paper, the precipitates are practically free from acid. It may be well to call attention to the fact that a first-class grade of filter paper should be used, otherwise the precipitate may run through the filter.

In Table II the results obtained when the solutions stood one-half and one hour and were then treated as above mentioned are compared with the gravimetric.

TABLE II.—COMPARISON OF TIME OF STANDING.

Stood one-half hour at 40°-50.					Stood one hour at 40°-50.				
Number.	Washings.	Percent stand- ing one-half hour.	Percent grav- imetric.	Difference + or — from gravi- metric.	Number.	Washings.	Percent. stood one hour.	Percent. grav- imetric.	Difference + or — from gravi- metric.
1	200	0.50	0.57	-0.07	1	200	1.84	1.75	+0.09
2	"	2.58	2.42	+0.16	2	"	1.96	1.79	+0.17
3	"	2.86	2.74	+0.12	3	"	2.38	2.38	0.00
4	"	2.06	2.17	-0.11	4	"	2.14	2.03	+0.11
5	"	2.10	2.17	-0.07	5	"	1.58	1.48	+0.10
6	"	5.00	5.06	-0.06	6	"	2.56	2.74	-0.18
7	"	4.41	4.56	-0.15	7	"	4.87	4.78	+0.09
8	"	3.06	3.08	-0.02	8	"	1.39	1.39	0.00
9	"	1.89	1.88	+0.01	9	"	2.08	2.07	+0.01
10	"	0.59	0.61	-0.02	10	"	2.88	3.06	-0.18
11	"	3.42	3.32	+0.10	11	"	2.40	2.54	-0.14
77	"	1.69	1.56	+0.12	12	"	3.43	3.25	+0.18
Average difference..... 0.085					13	"	3.18	3.33	-0.15
Difference of averages. +0.0016					14	"	1.42	1.39	+0.03
					15	"	1.01	0.91	+0.10
					Average difference..... 0.102				
					Difference of averages.. +0.015				

From these results it appears that standing as long as one hour before filtering does not give results differing from the gravimetric more than the allowance for duplicates by that method. These results are not what was to have been expected from Kilgore's<sup>1</sup> experiments with various molybdates, as he found that both the official solution and that used by Pemberton gave deposits of

<sup>1</sup> Bul. 43, Div. Chem. U. S. Dept. Agr., 103.

molybdc acid in less than half an hour when heated to 60°. This difference is possibly explained by the fact that the ratio of nitric acid to the molybdc acid in solution was much greater than in his experiments, due to the precipitation of most of the molybdc acid by the phosphoric acid present.

*B. THE EFFECT OF THE METHOD OF FILTERING AND WASHING AND THE USE OF TARTARIC ACID TO PREVENT THE PRECIPITATION OF MOLYBDC ACID.*

Jüpner's<sup>1</sup> experiments indicate that the precipitation of molybdc acid may be entirely prevented by the use of tartaric acid; also that the higher the temperature of precipitation the more tartaric acid required to keep the molybdc acid in solution.

Kilgore,<sup>2</sup> whose results are published since this work was done, comes to the conclusion that the use of citric acid for this same purpose possesses no advantage over the official molybdate solution, to which ten cc. of nitric acid per hundred has been added, and requires a much longer time for the complete precipitation of the ammonium phosphomolybdate.

In the work given below the official molybdate solution plus ten cc. nitric acid and one gram tartaric acid per 100 cc. was used. A very little work soon proved that adding the molybdate to the phosphate solution at 30°, and allowing to stand one hour at the temperature of the laboratory, will not give satisfactory results, and standing one hour at 30°, gave very little better results, the ammonium phosphomolybdate remaining in solution and precipitating some time after running through the filter. Standing over night in the cold, however, gave excellent results, on low percentages, upon which alone it was tried. It was next determined to try the plan of allowing solutions to stand at 40°-50° for one hour and for two hours; the results, which are in most instances, comparable with those obtained by the gravimetric method, are given, with the results by the method of allowing to stand over night, in Table III.

<sup>1</sup> Abs. Expt. Record, 6, 610.

<sup>2</sup> This Journal, 17, 960.

TABLE III.—COMPARISON OF TIME OF STANDING, USING MOLYBDIC SOLUTION CONTAINING TARTARIC ACID.

Stood one hour at 40°-50°.					Stood two hours at 40°-50°.					Stood over night in the cold.				
Number.	Washing.	Per cent. by molybdate containing tartaric acid.	Per cent. by volumetric.	Difference + or - from volumetric.	Number.	Washing.	Per cent. by molybdate containing tartaric acid.	Per cent. by volumetric.	Difference + or - from volumetric.	Number.	Washing.	Per cent. by molybdate containing tartaric acid.	Per cent. by volumetric.	Difference + or - from volumetric.
1	250	4.76	6.35 6.20	-1.51	1	275	1.40	1.33	+0.07	1	200	0.99	0.92	+0.07
2	"	2.54	2.38	+0.16	2	"	0.94	1.20	-0.26	2	"	2.14	2.16	-0.02
3	"	1.48	1.64	-0.16	3	"	0.65	0.50	+0.15	3	"	0.76	0.79	-0.03
4	"	2.41	2.57	-0.16	4	"	3.15	3.26	-0.11	4	"	1.35	1.32	+0.03
5	"	4.79	6.75 6.82	-2.00	5	"	2.77	2.58	+0.19	5	"	0.42	0.44	-0.02
6	"	1.81	2.28	-0.47	6	"	1.58	1.50	+0.08	6	"	1.70	1.65	+0.05
7	"	1.91	1.96	-0.05	7	"	2.20	2.08	+0.12	7	"	2.81	2.88	-0.07
8	"	2.22	2.06	+0.06	8	"	2.49	2.42	+0.07	8	"	1.12	1.12	0.00
9	"	0.72	0.69	+0.03	9	"	2.48	2.32	+0.16	9	"	1.56	1.49	+0.07
10	"	0.90	1.35 1.32	-0.44	10	"	2.28	2.40	-0.12	10	"	1.68	1.65	+0.03
					11	"	2.18	2.39	-0.19	11	"	1.18	1.10	+0.08
										12	200	2.52	2.45	+0.07

From these results it would appear that standing at 40°-50° for one hour is not to be relied on, at least for low percentages, the results in all cases being too low. Standing at 40°-50° for two hours, however, tends to give results slightly higher than those obtained by the volumetric method, while standing in the cold over night gives results practically identical with it.

This work of determining the temperature and time of standing that would probably give the best results, was done with low percentage solutions, as they were the most convenient at the time.

The figures so far obtained indicated that for further study with the official molybdate solution containing ten cc. of nitric acid extra, standing one-half hour at 40°-50°, was to be preferred, as standing for one hour tends to slightly high results. It is believed, however, that standing for one hour will still give results comparable with results by the gravimetric method, but the precipitates require more washing, and longer time is required to complete the determinations.

For the further study of the use of tartaric acid, standing at 40°-50° for two hours was selected.

For this final comparison of the various modifications solutions of fertilizers in which the phosphoric acid had been carefully determined gravimetrically by Mr. W. W. Skinner, were used. The samples cover practically all grades of commercial fertilizers, and have quite a range in percentage of phosphoric acid. The solutions and precipitates in both modifications were treated alike in all cases, except the time of standing.

TABLE IV.—COMPARISON OF VARIOUS MODIFICATIONS WITH THE GRAVIMETRIC.

Number.	One gram tartaric acid per 100 cc. molybdate two hours at 40°-50°.	Official molybdate + ten cc. HNO <sub>3</sub> per 100 cc. one-half hour at 40°-50°.	Gravimetric. (Skinner).	Volumetric.	Difference + or - from gravimetric. Tartarated. Molyb. date.	Difference + or - from gravimetric. Official molybdate + ten cc. HNO <sub>3</sub> per 100 cc.
1	9.73	9.68	9.75	....	-0.02	-0.07
2	15.65	15.35	15.34	15.45	+0.16	-0.01
	15.42					
	(12.85) <sup>1</sup>					
3	13.05	12.93	13.06	....	+0.04	-0.13
	13.15					
	6.60	6.48 <sup>2</sup>	6.30	....	+0.34	+0.16
4	6.68	6.43 <sup>3</sup>				
5	13.35	13.28	13.35	....	0.00	0.07
	10.00					
6	9.95	10.10	10.19	. . .	-0.21	-0.09
	(10.33) <sup>1</sup>	10.20				
7	17.10	17.03	17.40	16.93	-0.25	-0.31
	17.20	17.15				
8	17.70	17.60	17.94	17.65	-0.25	-0.29
	17.68	17.70				
9	22.08	22.10	22.29	22.15	-0.21	-0.19
	22.08					
10	20.95	22.68	20.85	....	+0.10	-0.07
		20.85				
Average	14.617	14.541	14.647		0.156	0.141
Difference of averages.....					-0.03	-0.10

In several instances where the modified methods gave decidedly lower results than the gravimetric method, the determinations were also made by the Kilgore modification, the results

<sup>1</sup> Omitted from averages.

<sup>2</sup> Fifteen cc. molybdate used.

<sup>3</sup> Ten cc. molybdate used.

agreeing in all cases with the results by the modified methods.

The results agree fairly well with the reported results by the Kilgore method, which averages slightly lower than the gravimetric results. The average difference by these modifications is 0.156 and 0.141 per cent., and the average of the plus and minus differences is 0.03 and 0.106 by the tartrated molybdate and by the Kilgore molybdate respectively.

Only two results are noticeably higher than the gravimetric, and only one of these differs by more than two-tenths per cent. This seems to be due to the presence of a great excess of molybdate, as it will be noticed that when less molybdate was used the result was nearer the gravimetric. From the observation of quite a number of results, the writer believes that the amount of molybdate added should not be more than enough to precipitate one and a half times the phosphoric acid found to be present, otherwise the results are too high.

From the figures presented the following conclusions may be drawn :

1. The molybdate solution, to which nitric acid has been added, standing one-half hour at 40°-50°, gives results comparing very favorably with the gravimetric.
2. While the use of tartaric acid in the molybdate solution gives good results, it possesses no advantage and the extra time of standing makes it not so desirable.

The official molybdate plus ten cc. nitric acid per 100 cc., using the funnel and paper without pressure in filtering, and only water for washing is preferred by the writer to the usual way of carrying out the volumetric method; this admits of a better distribution of the work, which makes it in his hands a more rapid method where a large number of determinations are to be made.

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INDEX TO THE LITERATURE ON THE DETECTION AND  
ESTIMATION OF FUSEL OIL IN SPIRITS.

By W. D. BIGELOW.

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## THE OCCURRENCE OF TITANIUM.

By CHARLES E. WAIT.

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IT is not my present purpose to repeat what has been already frequently published relative to the presence of titanium in minerals, typical rocks, meteorites, clays, soils, blast furnace products, etc. I wish merely to call attention to the fact that some of the bodies with which we have much to do contain titanium, and that probably owing to the difficulties formerly

experienced in its estimation, it has been more frequently overlooked than is generally supposed.

In the recent examination of food materials, under the direction of the United States Department of Agriculture, I have had occasion to make analyses of the ashes of some plant materials, and this having led to further investigations, I was interested and surprised to find titanium present in every plant ash thus far examined.

This is in fact surprising, as it is stated by some writers<sup>1</sup> that "it does not appear to form part of the animal or vegetable kingdom."

The amount of titanic oxide found in the ash of some vegetable material is as follows :

	Per cent.
Oak wood .....	0.31
Apple and pear wood mixed .....	0.21
Apple .....	0.11
Cow peas .....	0.01
Cottonseed meal .....	0.02

From the above determinations we are reasonably safe in assuming that titanium is assimilated by plants. If this is true, it seems very strange that reference to this fact has not been made by recent writers upon agricultural chemical analysis, and upon the chemistry of vegetable life.

In fact, in consulting treatises on ash analysis with tables,<sup>2</sup> I do not find any mention whatever of the presence of titanium. If this is a fact, can it be true that it has escaped the attention of chemists for so long a time ?

The examination of the ash of bituminous and anthracite coal shows the presence of titanic oxide. The results of some determinations are as follows :

	Per cent.
Jellico (Tenn.) bituminous coal .....	0.69
Coal Creek (Tenn.) bituminous coal .....	0.95
Pocahontas (Va.) bituminous coal .....	0.94
Middlesborough (Ky.) bituminous coal .....	0.83
Pennsylvania anthracite coal .....	2.59

<sup>1</sup> Roscoe & Schorlemmer,

<sup>2</sup> Wolff.

With reference to the presence of titanic oxide in the ash of coal, it may be fairly assumed that partly owing to the infiltration of clay and earthy materials, it would be found there, but is it fair to assume that its presence is wholly accounted for in that way? If mention has been made of the presence of titanium in the ash of coal, it has thus far escaped my attention.

The method employed in the above determination is that of A. Weller,<sup>1</sup> which is based upon the fact that hydrogen peroxide, when added to a solution of titanium, produces a compound of an intensely yellow color. There are precautions necessary in the execution of this method which have already been pointed out.<sup>2</sup>

It will be my pleasure to report additional notes at an early day concerning the presence of titanium in the vegetable kingdom. Valuable service has been rendered in the above work by Messrs. J. O. LaBach and C. O. Hill.

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## THE ESTIMATION OF PYRRHOTITE IN PYRITES ORES.

By EDWIN F. CONE.

Received January 22, 1896.

SOME of the American pyrites ores contain the mineral pyrrhotite ( $\text{Fe}_7\text{S}_8$ ) in varying proportions. In the manufacture of sulphuric acid from these ores it is found impossible to burn out at least the greater part, if not all, of the sulphur which is present as pyrrhotite. In the estimation of total sulphur in the sample of such an ore, of course the sulphur present as pyrrhotite is included. It is therefore necessary, in order to make a settlement with the company selling the ore and also in order to figure the yield of acid, to estimate the sulphur present as pyrrhotite as accurately as possible. Authorities give no method to meet the conditions. After a careful investigation of the matter I have perfected the following method; I am indebted to Mr. Lucius Pitkin, of New York City, for some valuable suggestions. It is based on the fact that  $\text{Fe}_7\text{S}_8$  is magnetic, pyrites being non-magnetic.

<sup>1</sup> *Ber. d. chem. Ges.*, 1882.

<sup>2</sup> This Journal, 13, 210.



*Method.*—After the ground sample has been passed through a sixty mesh sieve, 13.74 grams are weighed and spread out upon a good-sized sheet of glazed paper. A magnet is passed through and over this several times, the magnetic portion being carefully separated from the magnet by first stroking suddenly the top of the magnet, which dislodges most of the mechanically admixed pyrites, and then, secondly, separating the magnetic portion by means of the armature and a brush. The process is carried out five or six times, enough separations having been made to have reasonably separated all the magnetic portion. This is then finely ground in an agate mortar and the sulphur estimated gravimetrically by oxidation with nitric and bromo-hydrochloric acids. The weight of barium sulphate obtained in grams is the percentage of sulphur present as pyrrhotite.

The accuracy of this method was proved by the following work :

A sample of ore containing a known percentage of pyrrhotite was obtained. It analyzed as follows :

	Per cent.
Total sulphur .....	35.07
" iron .....	57.50
Oxygen as $\text{Fe}_3\text{O}_4$ .....	4.26
Copper .....	0.25
Insoluble matter .....	2.78
	<hr/> 99.86
Sulphur present as $\text{Fe}_7\text{S}_8$ .....	24.14
Iron " " $\text{Fe}_7\text{S}_8$ .....	36.96
" " " $\text{FeS}_2$ .....	9.34
Sulphur " " $\text{FeS}_2$ .....	10.68
Iron " " $\text{Fe}_3\text{O}_4$ .....	11.20

A sample of pyrites containing no pyrrhotite nor magnetic portion was then obtained. To a definite portion of this I added enough of the ore containing pyrrhotite to give 1.20 per cent of sulphur present as pyrrhotite in the mixture ; *i. e.*, to fifty grams of the pyrites I added 2.63 grams of pyrrhotite ore, or

$$\frac{24.14 \times 2.63}{52.63} = 1.20 \text{ per cent. sulphur as } \text{Fe}_7\text{S}_8.$$

This mixture was then analyzed for sulphur present as pyr-

rhottite by the method described above, using different weights. Some of the results obtained are :

5.00	grams	gave	0.4120	barium sulphate	=	1.13	per cent. sulphur as $\text{Fe}_2\text{S}_3$ .
13.74	"	"	1.1300	"	"	= 1.13	" " $\text{Fe}_2\text{S}_3$ .
25.00	"	"	2.1570	"	"	= 1.18	" " $\text{Fe}_2\text{S}_3$ .

Others were equally concordant.

The method was also applied to the pyrrhotite, as mentioned above, using portions of one gram or one-half gram giving respectively 24.13 per cent. and 24.15 per cent. sulphur as  $\text{Fe}_2\text{S}_3$ .

This method is accurate to within two-tenth per cent. on ores containing much or little pyrrhotite. The ore must not be finer than that which will pass through a sixty mesh sieve ; if it is, results will be unreliable.

Another method, which I used until the perfection of this one, is based upon the fact that  $\text{Fe}_2\text{S}_3$  gives off hydrogen sulphide with dilute acid, whereas  $\text{FeS}$ , (pyrite) does not. This is reliable when no other sulphides are present, but as most pyrites contain blende the results are usually unreliable.

CLEVELAND, O.

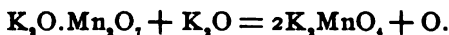
## DROWN'S METHOD OF DETERMINING SULPHUR IN PIG IRON.

BY GEORGE AUCHY.

Received February 26, 1896.

OF the various evolution methods of determining sulphur in pig iron, Drown's is perhaps the best. Methods in which the sulphur is precipitated in any other form but barium sulphate (cadmium sulphide for instance), are not so convenient for the reason that the sulphur in the graphitic residue must be determined as barium sulphate. A slight drawback, however, attaches to the method in that the evolution of the gas must not be allowed to proceed too rapidly, and it is an object of this note to point out that by the use of potassium hydroxide solution in conjunction with the potassium permanganate solution as an absorbent for the gas, this caution is made unnecessary, and the gas may be passed through the solution as rapidly as it is possible to make it do so, without danger of loss ; a mixed solution of caustic potash and potassium permanganate possessing stronger oxidizing power, than a solution of the latter salt alone. For there is a tendency in such a mixture, even

when no reducing agent is present, to the liberation of an atom of oxygen and a reduction of the potassium permanganate to potassium manganate, by the union of a molecule of potash with a molecule of potassium permanganate.



If a very large excess of caustic potash solution be added to a few drops of potassium permanganate solution, the reduction to green potassium manganate will be seen to take place immediately. But in a mixture of equal or nearly equal parts of the two solutions, the change is very slow and gradual, except a reducing agent be present.

Convenient proportions of the two solutions for use as an absorbent in the determination of sulphur in pig iron are obtained by using in each case six cc. of a caustic potash solution, made by dissolving six sticks of the solid hydroxide in 350 cc. water, and six cc. of a permanganate solution containing about ten grams of the crystallized salt to the liter of water.

These volumes of the two solutions are carefully withdrawn from the bottles containing them by pipettes, so as to avoid getting any of the sediment at the bottom of the bottle; mixed in a small beaker, and drawn into a Troilus bulb, which is then connected with the evolution flask containing the drillings. The solution of the pig iron may be accomplished in five or ten minutes without any hydrogen sulphide passing through the caustic potash and permanganate solution unabsorbed. The purple color of the permanganate gradually changes to the green of the manganate, which latter solution is also a stronger oxidizing agent than permanganate.

Not an inconsiderable convenience also in the use of this mixed solution is in the fact that the oxide of manganese separating out does not adhere to the glass tenaciously, and may be washed out with water instead of requiring to be dissolved out by strong hydrochloric acid and added to the main solution.

The next step in Drown's method is getting the manganese in colorless solution preparatory to the precipitation by barium chloride. This is accomplished by evaporation to dryness with hydrochloric acid, and separation of silica; or by adding enough hydrochloric acid to get the clear solution by the aid of heat, but

without the tedious evaporation to dryness, and afterwards neutralizing the excess of acid with ammonia. The writer would suggest the use of oxalic acid in connection with hydrochloric acid, as by its use the solution of the manganese oxides is effected almost instantaneously and without the use of an excess of hydrochloric acid, a very small amount of the latter sufficing, and the barium chloride precipitation may then at once take place.

In detail: Take 3.4335 grams of the pig iron drillings in a sixteen ounce gas flask and connect with the Troilius bulb containing the mixed solution of caustic potash and potassium permanganate, as described. Pour through the funnel tube dilute hydrochloric acid in not unnecessary amount, and bring quickly to a boil. Then push to a cooler part of the plate and aspirate air through. A convenient arrangement is to have a narrow upright board fastened to the desk, or on a stand next to the filter pump; on the other side of the board stands the iron plate. This upright board, standing edgewise to the plate, is provided with nails or hooks for the support of the Troilius bulbs which are hung one above the other. Three or four determinations can be carried on at once in this way with the greatest possible economy of desk room. The aspirating is done by the filter pump.

Transfer the contents of the Troilius bulb to a small beaker, washing out with water. Filter the solution in the evolution flask through a ribbed filter and wash with hot water. Then punch a hole in the paper and wash the graphite and silica into an evaporating dish. Evaporate to dryness. Add thirty cc. aqua regia. Evaporate to dryness. When dry, add eight to ten cc. dilute hydrochloric acid. Heat, dilute with hot water and filter into the solution washed out of the Troilius bulb. Bring this solution then to a boil, add enough oxalic acid to clear the solution, (a very little will suffice), then five cc. barium chloride solution and boil about an hour. Allow to stand over night. The barium sulphate found, multiplied by four, will give the percentage of sulphur in the pig.

Caustic potash solution always contains considerable amounts of dissolved silica (for instance, in six cc. the amount used in a determination was found to be 0.0051 gram). But it is not

necessary to separate it, as a recent writer in the *Chemical News* has shown that precipitated barium sulphate is not contaminated by silica in solution, and the following experiments also show it. In these experiments a standard solution of sulphuric acid was used; mixed in each case with the amounts of caustic potash solution, and permanganate solution that are used in a regular determination. Instead of using ten cc. of hydrochloric acid, however, twenty cc. was used, but afterwards made alkaline with ammonia, then hydrochloric acid added drop by drop till just acid again, and the solution filtered from the alumina remaining undissolved. Then precipitated by barium chloride. Also the excess of oxalic acid used to bring the manganese oxides into solution was destroyed by permanganate solution before the neutralization and precipitation and the slight excess of permanganate by a piece of fine iron wire and stirring. The barium sulphate found was, for convenience in each case, calculated as though the usual amount of drillings had been taken, and a regular determination had been made.

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1.....	0.237	0.238
" 2.....	0.121	0.119
" 3.....	0.057	0.057
" 4.....	0.029	0.033

To note the effect of precipitating in a strongly acid solution, and one which therefore required no filtration from alumina before precipitating, the following tests were made as before, but with ammonia added to leave five cc. of free hydrochloric acid at time of precipitation, (excess of oxalic acid again destroyed).

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1.....	0.121	0.112
" 2.....	0.121	0.114
" 3.....	0.237	0.234
" 4.....	0.057	0.054
" 5.....	0.029	0.029
" 6.....	0.014	0.010
" 7.....	0.029	0.028
" 8.....	0.029	0.026
" 9.....	0.014	0.010

These results show a very marked tendency to lowness. The following were then made, using ten cc. of hydrochloric acid for solution of the manganese oxides (together with oxalic acid, the excess of the latter however, afterward destroyed by adding permanganate solution), and without any after neutralization with ammonia whatever, the solution therefore containing *over* five cc. of free acid, but no ammonium chloride.

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1.....	0.014	0.014
" 2.....	0.029	0.029
" 3.....	0.121	0.115

At this point it was thought well to also try the effect of oxalic acid upon the precipitation. It was feared it might have a solvent action upon the barium sulphate, especially in strongly acid solutions. In other respects the conditions were the same as in the series immediately preceding—ten cc. hydrochloric acid, no ammonia, etc., but excess of oxalic acid *not* destroyed.

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1.....	0.014	0.014
" 2.....	0.029	0.029
" 3.....	0.121	0.118
" 4.....	0.029	0.029
" 5.....	0.060	0.059
" 6.....	0.090	0.090
" 7.....	0.045	0.046
" 8.....	0.060	0.060
" 9.....	0.090	0.090
" 10.....	0.029	0.029
" 11.....	0.014	0.014
" 12.....	0.121	0.119
" 13.....	0.237	0.239

From these results it would seem that the oxalic acid helped rather than hindered the precipitation of barium sulphate.

To see if there was any tendency of barium oxalate to precipitate, a test was made under conditions identical with No. 13, except that the solution was neutralized with ammonia till merely faintly acid before precipitating. Result 0.239 percent., or just the same as in the strongly acid test. Showing no tendency of barium oxalate to precipitate.

Again, in standard solution equivalent to 0.121 per cent. taken, ten cc. hydrochloric acid added, brought to a boil, and precipitated with barium chloride. Result 0.119 per cent. Then the test repeated twice with addition of oxalic acid. Results, No. 1, 0.120 per cent. ; No. 2, 0.120 per cent.

Thinking perhaps good results could also be obtained by allowing the precipitated barium sulphate to stand only one hour before filtration, the following tests were made (ten cc. hydrochloric acid, no ammonia, excess of oxalic acid not destroyed).

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1.....	0.029	0.024
" 2.....	0.014	0.007
" 3.....	0.029	0.023
" 4.....	0.121	0.115
" 5.....	0.060	0.056
" 6.....	0.045	0.041

Showing that one hour's standing is not sufficient. But the loss seems so uniform that in cases of hurry it would be perhaps safe to allow only one hour for standing, making afterward a correction in the result of 0.005 per cent.

It is important to make a blank or dummy test with the reagents used. In this test use double the reagents and precipitate in nearly neutral solution.

In the regular determinations also precipitations may of course take place in nearly neutral solutions if so desired, and as is usually recommended. The results of the second series, however, may perhaps be taken as a warning against the presence of ammonium chloride in *strongly* acid solutions, and the ammonia should therefore be added to near neutralization if used at all.

In filtering off the barium sulphate it is not advisable to use a rapid filtering funnel, as barium sulphate equal to 0.002 or 0.003 per cent. is more than likely to pass through the filter paper and escape notice in the filtrate, except the liquid be stirred in such a way as to collect it together in the middle of the bottom of the beaker. When hydrochloric acid is spoken of in this article the dilute acid (equal parts water and acid) is meant.

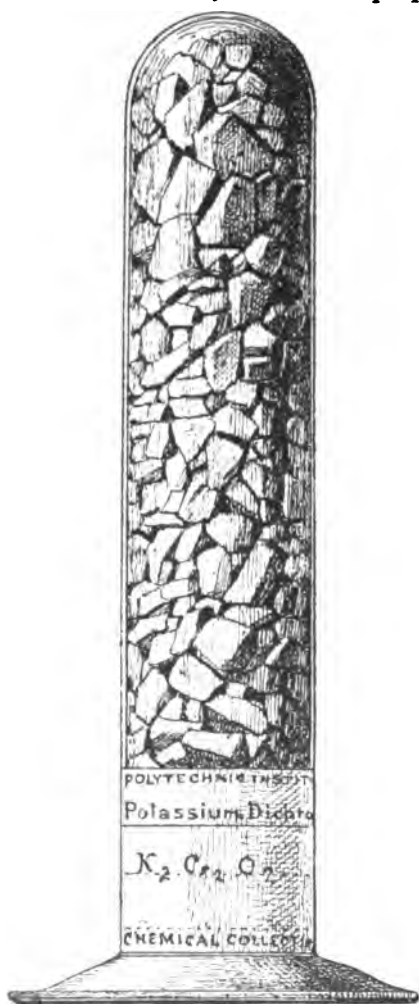
# NOTE.

*A New Specimen Bottle.*<sup>1</sup>—There are several reasons why glass-stoppered bottles are not well adapted for small specimens. The neck and stopper form an awkward looking cover to the specimen. The neck is usually too small in proportion to the width of the bottle,

and as a specimen is not intended to be taken out of its receptacle, the stopper and ground neck are inappropriate. But the chief objection to their use is their cost.

The form which I have found to be very practical consists of a tube with a rounded top provided with a flanged base. This form is pleasing to the eye, exhibits the whole of the specimen, is not easily upset, is air- and moisture-tight, and is low priced.

In filling the tube, it is inverted, and when enough of the specimen has been put in, a cylindrical (not conical cork) is pushed in. When the specimen does not pack, or when but few crystals are placed in the tube, it is well to paste a disk of white paper in the top of the cork, so as to conceal it from sight. In the case of colorless crystals, glazed black paper gives a better effect. The



FULL SIZE.

<sup>1</sup> Read before the New York Section, October 4, 1895.



cork should be driven in so as to leave about one-sixteenth of an inch space below the jointure of the tube and the flange. Melted paraffin is then poured in. A layer a quarter of an inch thick is quite enough to exclude air and moisture and to hermetically seal the tube. If desirable, the whole space of the base may be filled with paraffin, and, when cool, the wax may be pared down flat with a knife long enough to touch both sides. The addition of a little lampblack to the paraffin makes a better effect. The label is then put on. It should be long enough to give a slight lap and wide enough to cover the cork. The top of the cork should be just level with the edge of the label. The inside of the base flange may be painted with black varnish, or it may be made of black or colored glass.

The flanged base prevents the tubes from touching each other, and thus shows off the samples very effectively. It is well to arrange the shelves in stairs. The steps may be three inches wide and two and a half inches high. The rows should be alternate, so that the labels of each row but the first may be seen between the tubes of the row in front of it.

When a small amount or a single crystal of a specimen is to be exhibited, a good effect can be produced by thrusting a copper wire into the cork and twisting the other end into a circle about half an inch in diameter. On this is placed a three-fourths of an inch watch glass, and in this the specimen. The stalk of the support should be about two inches long. Other modifications will naturally occur to any one.

As the operations involved in making these specimens are few and simple, their cost is low in comparison with the ground glass-stoppered bottles. Whitall and Tatum make the size represented in the cut for \$7.00 a gross in four gross lots, which is a shade less than five cents a piece. Larger or smaller sizes can be furnished at proportional prices.

PETER T. AUSTEN.

## BOOKS RECEIVED.

The Smithsonian Institution ; Its Origin, Growth, and Activities. By Prof. Henry Carrington Bolton, Ph.D. New York : D. Appleton & Co. 30 pp.

Handbook of the Bio-Chemical Laboratory. By John A. Mandel. New York : John Wiley & Sons. v, 101 pp. Price, \$1.50.

Bulletin No. 28. An Important Elm Insect. Reno, Nev. : Agricultural Experiment Station of the Nevada State University. November, 1895. 8 pp.

Bulletin No. 29. The San Jose Scale. Reno, Nev. : Agricultural Experiment Station of the Nevada State University. December, 1895. 8 pp.

Bulletin No. 121. Hillside Terraces or Ditches. Raleigh, N. C. : North Carolina Agricultural Experiment Station. October, 1895. 8 pp.

Bulletin No. 125. Forage Grasses and Hay Making. I. Tests of Forage Grasses. II. The Formation and Care of Grass Lands. III. Haying Tools and Hay-Making. Raleigh, N. C. : North Carolina Agricultural Experiment Station. January 15, 1895. 41 pp.

Ueber Reindarstellung der Gährungsmilchsäure mit einleitenden Versuchen über Destillation in Vakuum der Quecksilberluftpumpe. Dissertation by Wilhelm A. Dyes, Ph.D. 1895. 44 pp.

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## ERRATA.

On page 223 (March number) under solution number 3, instead of

Water ..... 115 cc.

read

Water ..... 190 cc.

and instead of

Phosphoric acid 1.40 sp. gr. .... 315 cc.

read

Phosphoric acid 1.4 sp. gr. .... 340 cc.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### HYDROFLUORIC ACID.<sup>1</sup>

BY KARL F. STAHL.

Received March 20, 1896.

**H**YDROFLUORIC acid is always made by decomposing ground fluorspar with sulphuric acid in cast iron vessels and absorbing the resulting fumes of hydrofluoric acid in leaden vessels of varying construction, containing more or less water, according to the strength desired.

The commercial acid, containing forty to fifty-two per cent. hydrofluoric, is stored and shipped in lead vessels, or small quantities in gutta percha bottles. Weaker acid, of about thirty-five per cent. and less, can be stored for a limited time in wood and is sometimes shipped in barrels, usually oil barrels. In this country the so-called "chemically pure" acid is packed in ceresine bottles, which answer very well, but must be kept away from the Bunsen burner, as the melting point of the ceresine is low. In Europe the C. P. acid is shipped either in gutta percha or platinum bottles, but the acid takes up, in course of time, mineral and organic matter from the gutta percha and ceases to be C. P. Platinum bottles are the best, but require a heavy investment.

The impurities, which can hardly be avoided in manufacturing commercial hydrofluoric acid, and are therefore always present, are:

1. *Hydrofluosilicic Acid*.—This is the most important impurity,

<sup>1</sup> Abstracted from a lecture before the chemical section of the Engineers Society of Western Pennsylvania, at Pittsburgh, February 28th, 1896. Communicated by the author.

not because it does any direct harm in the application of the acid, but because the fluorine combined with silica is perfectly useless. The source of the hydrofluosilicic acid is free or combined silica in the fluorspar, which is all dissolved and volatilized by the hydrofluoric acid. It seems almost impossible to obtain spar free from silica. American ground fluorspar contains usually about one and a half per cent.; samples of English spar, which I have tested, were even higher in silica, about three per cent., while six samples of German spar contained from one-tenth to seven-tenths per cent. silica. In the rapid determination of silica in fluorspar an analytical problem presents itself, which I have not yet solved to my satisfaction. I use the following extremely simple method :

One gram of ground fluorspar, in a platinum dish, with a small platinum spatula, is dried at about  $130^{\circ}\text{C}$ ., weighed exactly, moistened with hydrofluoric acid, stirred with a spatula, evaporated to dryness on the water-bath ; this is repeated, then dried again at  $130^{\circ}\text{C}$ ., and weighed. The difference I assume to be silica, which is only correct when free silica is present, but the spar may contain silicates, for instance clay; in that case a fluoride of aluminum would be formed, part of the weight of the silica would be replaced by the weight of the fluorine retained and the silica be found too low. If carbonates are present the error would not be great, for instance,

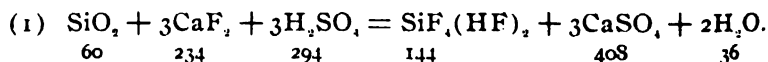
$\text{CaCO}_3$  (100) would give  $\text{CaF}_2$  (78),

and the silica be found too high. The presence of carbonate is, however, easily detected, and the carbonate can be removed with acetic acid. Galena is often present in small quantities and gives the spar a grayish or bluish color, in that case

$\text{PbS}$  (239) would give  $\text{PbF}_2$  (245),

an error that would not be perceptible. This simple method, to which any careful boy can be drilled in a short time, is therefore likely to give quite accurate results.

The great damage done by silica in the spar is plainly shown by the following equation :



For every part of silica about four parts of fluorspar and five parts of sulphuric acid are wasted, or expressing it in money value, for every per cent. of silica at least ten per cent. (four per cent. for spar and about seven per cent. for sulphuric acid) should be deducted from the value of the spar.

2. *Sulphuric Acid*, which is distilled over in small quantities out of the decomposing vessel, does no harm in the application of the hydrofluoric acid for etching glass or pickling iron. But in analyzing the acid it must be determined, otherwise it would be figured as hydrofluoric acid.

On evaporation and calcining, commercial acid should leave but a trace of non-volatile matter.

About five years ago, having made some hydrofluoric acid in an experimental apparatus, I was confronted with the inability to tell what I had made; that is, I could not find a method which would have enabled me to determine the composition in a reasonably short time.

The method of determining quickly the percentage of a liquid by its specific gravity is of little value for two reasons, first, because the methods for determining the specific gravity of other liquids can only be used with modifications for hydrofluoric acid, as they involve the use of a glass instrument of some kind. A glass hydrometer can only be used a few times until the acid has ruined it; picnometers are out of the question; even the temperature of hydrofluoric acid cannot be determined directly with a thermometer, as soon as a glass thermometer is placed into the acid the mercury begins to rise from the heat evolved by the action of the acid on the glass. I use, therefore, a platinum hydrometer. A hydrometer made from pure silver would probably last a long time. I have seen one made out of German silver plated with silver, but the hydrofluoric acid got through the plating and ate numerous pinholes into the instrument.

The impurities mentioned above, *i. e.*, hydrofluosilicic acid and sulphuric acid, influence the specific gravity of the hydrofluoric acid to a marked degree, so much that the determination of the specific gravity of an acid of unknown origin is of little value, but for controlling the process in the works, where the

character of the raw materials and the degree of purity of the produced hydrofluoric acid is known, it is of value, provided the conclusions drawn from it are from time to time verified by an analysis. It will not do to depend too much on the specific gravity.

Without taking up any time with a description of the experiments, which led finally to the method I use, I will give the latter in detail.

The samples are brought to the laboratory in lead cylinders of convenient size, with a handle. These are placed in water of  $15^{\circ}\text{C}.$ , often remaining there for at least five minutes; the specific gravity is taken; then with the aid of a small platinum tube, serving as a pipette, and chips of filtering paper, to remove a small excess, three portions are weighed out:

1. Two grams in a very small platinum crucible (holding about five cc).
2. Two grams in a large platinum crucible (holding about forty cc.)
3. Four grams in a small platinum dish.

#### A. TOTAL ACIDITY.

Place the small platinum crucible, covered with its lid, in a large platinum dish (holding about 100 cc.), then run, according to the expected percentage, twenty-five or fifty cc. normal caustic solution (forty grams caustic soda per liter) from a pipette into the dish, upset the covered crucible, and mix the acid and alkali with a platinum stirrer; add two drops of a solution of phenolphthalein (1 gram in 100 cc. alcohol) and then add more of the normal soda solution from a burette till the colorless liquid assumes the characteristic bright red color. Place over a Bunsen burner and heat to about  $50^{\circ}\text{C}.$ ; the red color will disappear. Finally add normal solution from the burette slowly till the red color remains constant when heated, which indicates that all free sulphuric acid, hydrofluoric acid, and hydrofluosilicic acid have been neutralized. The number of cubic centimeters used we call "*a.*"

If litmus is used in place of phenolphthalein, the soda solution has to be added till the color is perfectly blue, but the end of the

reaction is indistinct, while with phenolphthalein as indicator it is very sharp.

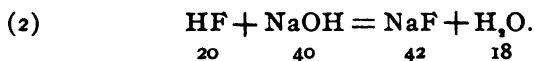
#### B. HYDROFLUOSILICIC ACID.

To the acid in the large platinum crucible (two grams) add five cc. water (measured approximately), then slowly about two grams<sup>1</sup> potassium carbonate either in small pieces or in concentrated solution, add about fifteen cc. of fifty per cent. alcohol and then as many cubic centimeters of ninety-five per cent. alcohol as water used, which will bring the whole to a volume of about twenty-five cc. containing about fifty per cent. alcohol,<sup>2</sup> let it stand for at least one hour. Filter<sup>3</sup> and wash the gelatinous precipitate, consisting of potassium silicofluoride, with fifty per cent. alcohol till blue litmus paper ceases to be turned red by the filtrate. Throw the filter with the precipitate into a platinum dish, add about twenty-five cc. of water and warm to about 50° C., titrate slowly with normal caustic soda solution and phenolphthalein, as described in the determination of total acidity. The number of cubic centimeters used we call "b."

#### C. SULPHURIC ACID.

Place the platinum dish containing four grams of the acid to be tested, on a water-bath under a hood with a good draft and evaporate till acid fumes have completely ceased to be given off. Titrate the remaining syrupy liquid, which contains the free sulphuric acid, cold, with normal acid solution, using either litmus or phenolphthalein as indicator. The number of cubic centimeters used we call "c."

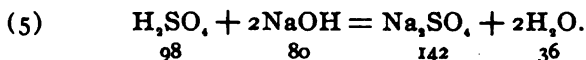
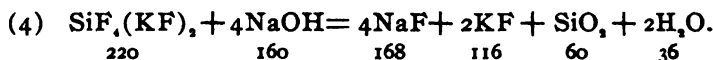
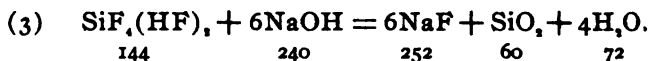
The reactions involved are as follows :



<sup>1</sup> The amount of potassium carbonate is calculated to neutralize the acids only partly. To avoid an excess it is advisable to test the liquid with litmus paper, which should show a strong acid reaction. But there should be at least enough potash to form potassium silicofluoride with the fluosilicic acid. In analyzing acid of entirely unknown composition I take for every cubic centimeter normal soda solution used for the determination of total acidity 0.05 gram potassium carbonate. Potassium chloride might be used in place of the carbonate, but in that case free hydrochloric acid is formed, in which the potassium silicofluoride is somewhat soluble.

<sup>2</sup> If the liquid contains more than fifty per cent. alcohol, potassium fluoride is precipitated, if much less alcohol, potassium silicofluoride may remain in solution.

<sup>3</sup> I use a platinum funnel because glass funnels are acted on, but that does not influence the accuracy of the method.



Now the number of cubic centimeters of normal soda solution used in the first titration and called "*a*" represents the alkali necessary to neutralize the hydrofluoric acid, hydrofluosilicic acid, and sulphuric acid, and in order to find the number of cubic centimeters used for hydrofluoric acid alone, we have to subtract those used for hydrofluosilicic acid and sulphuric acid, but although we used the same weight (two grams) for the determination of the hydrofluosilicic acid, it would not be correct to subtract the number of cubic centimeters used, because in the potassium silicofluoride two atoms of fluorine are neutralized and we only neutralize with normal solution the remaining four atoms, which are combined with silicon. It would therefore have required  $b + \frac{b}{2}$  cc. to neutralize the free acid.

Having employed four grams of substance for the determination of the sulphuric acid, the number of cubic centimeters used for that determination must be divided by 2. The number of cubic centimeters used for hydrofluoric acid alone are therefore equal to  $a - (\frac{3}{2}b + \frac{c}{2})$  and as each cubic centimeter normal solution indicates 0.020 gram HF and two grams of substance have been used, the number of cubic centimeters found by the above formula express, without further calculation, the percentage of free hydrofluoric acid. Therefore

$$a - (\frac{3}{2}b + \frac{c}{2}) = \text{per cent. free hydrofluoric acid.}$$

After the foregoing explanation the calculation of the percentage of hydrofluoric acid is an easy matter. One cc. normal sodium hydroxide indicates 0.055 gram potassium silicofluoride, which was obtained from 0.036 fluosilicic acid; having used two grams of substance, 0.036 has to be divided by 2 and multiplied by 100 to get the percentage, or

$$b \times 1.8 = \text{per cent. hydrofluosilicic acid.}$$



The percentage of free sulphuric acid is obtained by multiplying  $c$ , the number of cubic centimeters used, by 0.048, dividing by 4 and multiplying by 100, or

$$c \times 1.2 = \text{per cent. free sulphuric acid.}$$

Other free acids, muriatic or nitric acid, which influence the accuracy of the determination, are not likely to occur in commercial hydrofluoric acid and their presence can easily be detected by well-known analytical methods:

To give an idea of the composition of some of the makes of hydrofluoric acid, I have appended a few of the analyses made in the course of five years:

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Specific gravity.....	1.299	1.264	1.253	1.244	1.264	1.282	1.247	1.234	
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Hydrofluoric acid....	39.6	42.2	44.3	48.1	48.6	51.1	54.2	48.6	33.5
Hydrofluosilicic acid..	2.7	14.9	10.1	4.7	5.0	6.8	8.1	6.3	10.6
Free sulphuric acid...	0.8	0.8	4.0	1.9	1.4	1.2	0.8	1.6	

1. Oct. 1891. Baker & Adamson, C. P. acid in ceresine bottle, 0.005 per cent. non-volatile residue.

2. Oct. 1891. Manufactured by J. C. Wiarda, sample received.

3. Nov. 1891. " " " " sample taken from package of 100 pounds.

4. Jan. 1892. Manufactured by James Irwin & Co., sample of lot of 3500 pounds.

5. Mar. 1892. Manufactured by James Irwin & Co., sample of lot of 3400 pounds.

6. Jan. 1894. Manufactured by Bender & Aldred, sample taken from package of 100 pounds.

7. Jan. 1895. Manufactured by James Irwin & Co., sample taken from tank holding 3000 pounds.

8. Oct. 1895. Manufactured by James Irwin & Co., sample taken from tank holding 3200 pounds, 0.015 per cent. non-volatile residue.

9. Jan. 1896. So-called "pickling acid" sample received from a foundry.

By comparing analyses Nos. 2 and 7 it can be seen what influence hydrofluosilicic acid has in raising the specific gravity; although No. 2 has a higher specific gravity than No. 7, it contains twelve per cent. less hydrofluoric acid, but six and eight-tenths per cent. more hydrofluosilicic acid. Nos. 3 and 6 have the same specific gravity, but No. 6 contains six and eight-tenths per cent more hydrofluoric acid and three and there-

tenths per cent. less hydrofluosilicic acid. The influence of sulphuric acid on the specific gravity can be seen by comparing Nos. 4 and 5.

A great difficulty in the manufacture of hydrofluoric acid is the very disagreeable and dangerous nature of the gaseous and liquid acid. The effects of the fumes on the respiratory organs are more injurious than those of other acids. Still more marked are the effects of the liquid acid on the skin. One drop of acid, although it does not make itself felt for a few hours, will, even on the horny skin of a workman's hand, cause a very painful inflammation in one-half day. Against the fumes the workmen protect themselves by respirators, or by the simpler way, which they usually prefer, of tying a handkerchief over nose and mouth and by greasing the unprotected parts of the face with lanolin. The latter is as effective as vaseline and easier to wash off. Against liquid acid rubber gloves afford protection. If liquid acid comes in contact with the skin it should be washed off at once with water and aqua ammonia, or another alkali, which will prevent injury.

In conclusion, I wish to say a few words about the different applications of commercial hydrofluoric acid.

The oldest, and up to the present time, most extensive application is for etching glass. For this purpose it can be applied in three different ways. In the gaseous form by suspending the articles to be etched over a mixture of fluorspar and sulphuric acid. This is the oldest way of etching and I believe most burettes, graduated cylinders, etc., for laboratory use are still marked in this way. If applied in gaseous form the acid leaves the surface opaque, while the liquid acid leaves the surface smooth and transparent. For the production of an opaque surface with liquid acid many empirical formulas are published and every glass factory, or rather every etching boss, has his own secret formula. But they all aim to produce a mixture of hydrofluoric acid with a fluoride of ammonium, or potassium, or sodium, with which a number of other substances such as sulphuric, acetic, or muriatic acids, or ammonium or potassium sulphate, etc., are mixed, but it seems quite unnecessarily. Hydrofluoric acid prepared for etching opaque goes under the trade name of

"white acid." Lead glass is very rapidly and uniformly etched and acid of forty-five to forty-eight per cent. is usually employed, while lime glass requires a stronger acid and more time. Lately, acid as strong as fifty-two per cent. HF is employed. "White acid" is much more convenient for application than gaseous acid and acts very rapidly; for instance, a lead glass lamp chimney can be rendered opaque by simply dipping it into the acid for one minute. Lime glass, even with acid specially prepared for it, requires about two minutes immersion. It is important that the temperature of the acid and the glass should be about  $15^{\circ}\text{C}$ . Parts of the glass which are to remain unetched, must be protected. For this purpose a number of substances are in use. Asphaltum varnish is usually employed, when the design is printed on paper and then transferred to the glass; for the so-called needle work a mixture of Burgundy pitch and beeswax is used.

A more recent application of hydrofluoric acid is for cleaning castings from sand. These have so far been cleaned, either by mechanical means, or with sulphuric acid, but the first is expensive and neither way, in many cases, satisfactory. The sulphuric acid loosens the sand by dissolving the iron to which it is attached, while hydrofluoric acid dissolves the sand itself and therefore acts more promptly and does not cause any loss of iron. It also dissolves the magnetic oxide formed on the surface of the iron very readily, much more so than sulphuric acid. This latter point is important for castings, which have to be worked afterwards with edged tools, the magnetic oxide being very hard. For cleaning castings, the acid is diluted to about one or two per cent. HF, the pickling can therefore be carried on in wooden vessels.

Some of the firms, who use hydrofluoric acid for cleaning iron, have kindly sent me reports on it. The most interesting parts of these reports I will mention here with their permission:

Mr. S. H. Stupakoff, Supt. Union Switch and Signal Co., writes:

"We use the acid in the proportion of two and one-half quarts to one-half barrel water, containing about twenty-five gallons,"—(equal to one pound forty-eight per cent. hydrofluoric acid

in thirty-five pounds of water, the liquid would therefore contain one and four tenths per cent. HF)—“The bath is filled to the top with castings and they are left in it for about half an hour. We can renew our charge by adding each time one quart of acid.

“We find that the hydrofluoric acid is vastly superior to sulphuric acid, as the latter will not pickle satisfactorily in less than one day, and besides this we use about double the quantity of sulphuric acid compared with hydrofluoric acid to pickle the same amount of castings.”—(as the quantities given by Mr. Stupakoff are by volume, this would be equal to one pound of ninety-three per cent. sulphuric acid in eleven pounds of water, the liquid would therefore contain eight and a half per cent. sulphuric acid, or six times as much as the hydrofluoric acid bath.)

“With the sulphuric acid we experienced a great deal of trouble by obtaining a white sediment on the castings, which was very difficult to remove, even when washed in hot water. This white coating would frequently work through the paint, with which the castings were subsequently covered.

“We had no occasion to try this acid for cleaning any other material but cast iron, with the exception of one instance, when we tried to remove heavy coatings of rust from a lot of mixed material, consisting of cast iron and wrought iron. The hydrofluoric acid did this to perfection and left a perfectly bright surface.

“I can say, in conclusion, that I am perfectly satisfied, that the use of hydrofluoric acid for the cleaning of new castings and corroded iron is certainly a success, and I will always prefer it to the old method of pickling in sulphuric acid.”

From the engineer of another firm I received the following report:

“The best solution is one to thirty”—(this is by volume, and the bath would contain, as he used forty-eight per cent. hydrofluoric acid about two per cent. HF)—“As we make no small castings of gray iron I have only used the acid on malleable castings, with the result that small castings are cleaned excellently in two hours. I have also cleaned castings in a mixture of one acid to fifty water”—(the bath would contain about one per

cent. HF)—“by leaving them in over night, but we prefer to clean with the stronger acid. The pickling vat is usually filled up with castings three times before it requires more acid.

“It takes sulphuric acid twice as long with the same proportion”—(that is, one to thirty would give a solution of about five and six-tenths per cent. sulphuric acid)—“and then does not eat into the corners as well as hydrofluoric acid; also wastes more iron and does not leave it bright.”

For iron which is to be enameled, the cleaning with hydrofluoric acid is also advantageous, because it leaves a purer metallic surface than can be obtained with other acids.

I am informed that a large firm in this city is at present making arrangements with a view of throwing out their whole mechanical cleaning plant, in which they have been cleaning sixty tons a day.

Hydrofluoric acid or its salts are also used in distilleries to insure a more complete fermentation.<sup>1</sup>

The latest application, of which I heard only a few days ago, is for cleaning out oil and gas wells. It seems that the shooting of a well sometimes packs the rock so tightly that the hole is dryer after the shooting than before. By pouring about six barrels of hydrofluoric acid (I suppose the acid is used diluted) into the hole, which dissolves the silicates and afterwards is pumped out again, gas or oil get an outlet.

## NITROGEN ASSIMILATION IN THE COTTON PLANT.

BY CHARLES E. COATES AND W. R. DODSON.

Received March 3, 1896.

**I**N the spring of 1895, while looking up the literature of the cotton plant, it was noted that no quantitative work could be found touching the question of nitrogen assimilation in any member of the mallow family. As the cotton plant is highly nitrogenous in character and as there seemed to be no reason why the leguminosae should have a preemption claim on the absorption of free nitrogen, it was decided to undertake certain experiments along these lines, following Hellriegel's methods as far as possible, in the hope that something of importance might

<sup>1</sup> Article of Dr. Leo Backeland, this Journal, 14, 212.

be discovered concerning the relationships of cotton to atmospheric nitrogen. The conclusions of these experiments, however, were so entirely negative that this hope has been abandoned, and while, perhaps, they have not disproved the point in question absolutely, still it has been decided to put them on record in the belief that they afford at least strong evidence that cotton does not follow the legumes in this respect.

The method of work was as follows: A quantity of white sand was sifted through a one and a half mm. sieve, heated red hot in an iron pan and washed first with ordinary artesian water and afterwards with nitrogen-free water. Ten grams gave no nitrogen when analyzed by the usual Kjeldahl method. Ordinary flower pots were used, holding each about six pounds of sand. The sand had a water-holding capacity of about twenty-three per cent. It was kept moist to the extent of about seventy-five per cent. of its maximum capacity. The water used was obtained from artesian water nearly free from ammonia by distilling it and collecting only the middle third of the distillate.

• It gave merely traces of ammonia with Nessler's solution when analyzed in the usual way. A number of cotton seeds were linted as thoroughly as possible. The average weight of fifty-one seeds was 0.1166 gram. Of these, thirty-eight were weighed accurately and the weights of twenty fell between 0.110 gram and 0.130 gram. These twenty were soaked twenty-four hours in pure water, placed on moist sand in a dish, covered with a piece of filter paper, and the dish covered with a glass plate. As soon as a normal germ and rootlets appeared the seeds were planted in the pots, only those seeds being selected which showed about the same germinative energy. Before planting, four cc. of each of the following solutions were added to certain pots: potassium phosphate, 136 grams to liter; magnesium sulphate, 120 grams to liter; potassium chloride, 74.5 grams to liter; and calcium chloride, 70.8 grams to liter. The seeds were planted about three-quarters of an inch deep in the sand and the pots were covered with cotton wadding until the plant appeared. They were kept in the open air and put under cover whenever it threatened rain. On one occasion a small quantity of rain fell on the pots. Otherwise they received only nitrogen-

free water. The seeds were all planted on the first of May.

*Pot 1.*—No nutriment was added to this pot. The plant was dead by May 18.

*Pot 2.*—Same as 1. The plant was dead by May 28th.

The growths were so little in 1 and 2 that no analyses were made. To 3, 4, 5, 6, and 7 the solutions mentioned before were added. They were mixed, diluted to about 500 cc., mixed thoroughly with the sand in a porcelain dish and transferred to the pot before the seed was planted. After the plants had been growing a week or so, to 5, 6, and 7 there were added twenty-five cc. of a soil infusion, made as follows: A quantity of earth was taken from a field which had been planted in cotton for ten or twelve years. This earth was mixed thoroughly and 200 grams were shaken with one liter of water. After standing an hour or so, the clear supernatant liquid was decanted. A nitrogen determination gave 0.0002 gram nitrogen to twenty-five cc. of this liquid. It was applied by a pipette to the roots of the plant while in the pot. The assumption was that any bacterial agencies which might affect the cotton plant would surely be present in the soil of the old cotton field. A similar method had proved efficacious in innoculating legumes.

*Pot 3.*—With mineral food—without soil infusion. The plant died about the last of May, apparently of nitrogen starvation.

*Pot 4.*—Same as 3. The plant lived until the close of June, but growth had ceased by June 15. June 27 this plant and plants 5, 6, and 7, were removed from the pots and analyzed as follows: The sand was washed carefully from the roots, the entire plant was dried at 100°, and the nitrogen determined by the Kjeldahl method. In this case the seed weighed 0.1300 gram. A series of analyses had given 3.07 per cent. nitrogen in the whole cotton seed.

	Gram.
Nitrogen in seed of 4 . . . . .	0.004
Dry matter in seed of 4 . . . . .	0.5050
Nitrogen found in seed of 4 . . . . .	0.0068

*Pot 5.*—With mineral food, plus soil infusion.

	Gram.
Seed weighed.....	0.1244
In seed nitrogen.....	0.0038
Dry matter.....	0.4768
Nitrogen found.....	0.0056*

*Pot 6.*—Same as 5.

	Gram.
Seed weighed.....	0.1285
In seed nitrogen.....	0.0039
Dry matter.....	0.8350
Nitrogen found.....	0.0074

*Pot 7.*—Same as 5 and 6.

	Gram.
Seed weighed.....	0.1175
In seed nitrogen.....	0.0036
Dry matter.....	0.9664
Nitrogen found.....	0.0080

In all these instances growth had stopped before the plants were removed from the pot. The gain in nitrogen without soil infusion was 0.0028 gram; with soil infusion, 0.0018, 0.0035, and 0.0044 gram. Apparently it mattered very little whether the soil infusion was added or not and in all the instances the gain was so inconsiderable as to lie well within the limits of error of the experiments. It would seem therefore that under the conditions employed the cotton plant does not assimilate atmospheric nitrogen.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, No. 19.]

### DETERMINATION OF LACTOSE IN MILKS BY DOUBLE DILUTION AND POLARIZATION.

By H. W. WILEY AND E. E. EWELL.

Received March 20, 1896.

**I**N volume 6, page 289, of the *American Chemical Journal*, one of us (Wiley) published an article on the determination of lactose in milks by optical methods. The principal novelty in this process was the substitution of mercuric nitrate as the reagent for precipitating proteids in place of the other reagents which had usually been employed for that purpose. By the use of mercuric nitrate in an acid solution, it was shown in that



paper that it was possible to practically throw out all of the proteid dissolved in the milk. Inasmuch as these soluble proteids are optically active, and deflect the plane of polarization in a direction opposite to that produced by lactose, the presence of any notable quantity of them in the solution to be polarized tends to diminish the apparent percentage of lactose present. The reagent proposed, *viz.*, acid mercuric nitrate, when used in the cold and in the quantities specified, produces no inversion effect whatever upon the lactose.

In the paper referred to an arbitrary correction was made for the volume of the precipitate produced and this was fixed at two and five-tenths cc., when approximately sixty cc. of milk were used in a 100 cc. flask.

This method of estimating lactose on account of the ease with which it can be operated and its accuracy has been generally adopted by chemists. Attention has been called, however, to the fact that the arbitrary correction allowed for the volume of the precipitate is too small.<sup>1</sup>

Theoretically, it is evident also that the arbitrary correction admitted is too small except in cases of well-skimmed milk. In order to eliminate this arbitrary factor from the method, we undertook a series of experiments to determine the actual percentage of sugar and the proper correction to be allowed for the volume of the precipitate by the method of double dilution and polarization originally proposed by Scheibler for sugar solutions, and suggested by Bigelow and McElroy for use in the polarization of milk sugar.<sup>2</sup> The results of our determinations are extremely satisfactory, and show that the volume which is occupied by the precipitate in a milk varies from two and a half cc., in the circumstances mentioned above, to six cc., according to the richness of the milk in fat. It appears, however, that this correction is less in quantity than the apparent combined volume of the fat and albuminoids which may be safely assumed to be one cc. for one gram.

All the flasks which were employed in the determinations were carefully calibrated, and the instrument used was the new triple-field shadow polariscope, made by Schmidt and

<sup>1</sup> *Analyst*, 12, 64; 20, 126.

<sup>2</sup> *This Journal*, 15, 694.

Haensch, which enables readings to be accurately made to within 0.05 per cent. All readings were made in duplicate by each of us and entered before comparisons were made, and in the polarizations given in the table the means of these four readings, which never differed by more than one tenth per cent., are given. The polarizations were made on the contents of a 100 and a 200 cc, flask, after clarification of the milk by means of acid mercuric nitrate. In each case, double the quantity of the normal weight of milk for the instrument used was taken. The readings were calculated by the formula given by Scheibler, which requires that the reading obtained from the solution in the large flask be multiplied by two and subtracted from the reading obtained in the small flask. In all cases, in order to secure greater accuracy, our readings were made in a tube 400 mm. in length. Therefore, the data obtained in reading the solution in the small flask were divided by four in order to obtain the apparent percentage of sucrose.

The application of the formula given by Scheibler does not give absolutely accurate results. The true polarization in any given case is calculated according to the following scheme:

Let  $x$  equal the volume of the precipitate and  $y$  the correct reading. Let  $a$  equal the reading obtained from the solution in the small flask and  $b$  equal the reading of the solution from the large flask. We then have

$$\begin{aligned} 200 - x : 100 - x &:: a : b \\ 200b - bx &= 100a - ax \\ ax - bx &= 100a - 200b \\ x &= 100 \frac{(a - 2b)}{a - b} \dots \dots \dots (1) \end{aligned}$$

$$\begin{aligned} 100 - x : 100 &:: y : a \\ 100 - 100 \frac{(a - 2b)}{a - b} &: 100 :: y : a \end{aligned}$$

$$100 \left( a - \frac{a(a - 2b)}{a - b} \right) = 100y$$

$$y = a - \frac{a(a - 2b)}{a - b}$$

$$y = \frac{a^2 - ab - a^2 + 2ab}{a - b} = \frac{ab}{a - b} \dots \dots \dots (2)$$

The rule derived from formula No. 2 is as follows:

The true polarization, as determined by double dilution, is found by dividing the product of the two readings made from the solutions in the large and small flasks by their difference.

In order to test the accuracy of the method, known volumes of insoluble material, as, for instance, quartz sand, were added to the flasks in order that the volume of the precipitate might be increased by a certain definite amount. The determinations were also made on the whole milk as purchased, on the same milk deprived of the most of its cream and on the cream thus secured. In all cases the results obtained were perfectly satisfactory.

Blyth has lately described a method of precipitating the casein with acid and of washing the precipitate free of sugar on a filter and polarizing the filtrate.<sup>1</sup> The percentage of milk sugar in the mixed filtrate and washings is about one and the polariscopic reading should be corrected for that degree of dilution. This method evidently is better suited for preparing milk whey for the gravimetric estimation of the sugar by copper, since it takes no account of the albumens still in solution and serving to a certain extent to counteract the polarizing power of the lactose.

In the presence of sucrose he proposes to estimate its quantity from the property possessed by citric acid of inverting the sucrose and leaving the lactose unchanged. Raumer and Späth<sup>2</sup> suggest that the polarization of milk should be preceded by boiling, since it is probable that the lactose may exhibit birotation. The data which they adduce, however, are far from convincing, since after the boiling they clear the mixture with lead subacetate and it has been shown that this reagent does not remove all the proteids. The deficit in rotation is therefore probably due to the residual soluble left-handed proteids. They further suggest that the presence of a dextrinoid body, as indicated by Ritthausen<sup>3</sup> may serve to increase the actual rotation of the milk sugar. In the samples which showed the apparent

<sup>1</sup> *Analyst*, 20, 122.

<sup>2</sup> *Ztschr. angew. Chem.*, 1896, 72.

<sup>3</sup> *J. prakt. Chem.* (2), 15, 348.

increase, however, they made no attempt to prove the presence of the alleged disturbing dextrin.

There seems to be no just reason, therefore, for insisting on the slow and tedious gravimetric method when a quick and accurate optical method is at hand.

Inasmuch as the time required for carrying out the method of double dilution and polarization is scarcely any longer than that required for a single polarization, it is recommended that it be done in all cases, instead of correcting the results of a single polarization by any arbitrary factor. When the determination is conducted as suggested, the analyst has at hand an easy, rapid, and accurate method of estimating milk sugar in milk, which is as desirable in all respects as any gravimetric method whatever. The data obtained are given in the accompanying table.

POLARIZATION OF MILK BY DOUBLE DILUTION.

No.	Per cent. fat.	Polariza- tion in 200 cc. flask.	Polariza- tion in 100 cc. flask.	Apparent lactose. per cent.	True lactose. per cent.	True vol- ume in 100 of pre- c. flask.	Volume cipitate.
1	....	9.37	19.26	4.82	4.56	94.4	5.6 <sup>1</sup>
2	....	9.59	20.33	5.08	4.54	88.8	11.6 <sup>2</sup>
3	....	9.36	19.20	4.80	4.57	95.0	5.0 <sup>2</sup>
4	....	9.60	20.25	5.06	4.56	89.7	10.3 <sup>4</sup>
5	2.9	10.15	20.84	5.21	4.95	94.8	5.2
6	4.8	10.31	21.21	5.30	5.00	94.5	5.5
7	3.1	9.49	19.41	4.85	4.64	95.7	4.3 <sup>5</sup>
8	4.0	10.01	20.45	5.11	4.90	95.9	4.1
9	1.4	9.44	19.26	4.82	4.63	96.1	3.9 <sup>6</sup>
10	5.5	11.05	22.68	5.67	5.38	94.8	5.2
11	4.4	9.57	19.47	4.87	4.71	96.5	3.5 <sup>7</sup>
12	2.0	9.75	19.93	4.98	4.77	95.8	4.2 <sup>2</sup>
13	17.6	8.72	19.13	4.78	4.01	82.4	17.6 <sup>9</sup>

*Summary of Method.*—For the scale of the instrument used, 32.91 grams of pure lactose in 100 cc. give a reading of 100. This number is derived from the following data: For sucrose concentration twenty-five grams in 100 cc.,  $[\alpha]_D^{20} = 66.37$ .

<sup>1</sup> Without sand.

<sup>2</sup> With five cc. quartz sand.

<sup>3</sup> Without sand.

<sup>4</sup> With five cc. quartz sand.

<sup>5</sup> Same as No. 6, after separation of cream.

<sup>6</sup> Same as No. 8, after separation of cream.

<sup>7</sup> Whole milk.

<sup>8</sup> Skimmed milk.

<sup>9</sup> Cream.

For lactose, thirty-three grams in 100 cc.,  $[\alpha]_D^{20} = 52.53$ ; then  $66.37 : 52.53 :: x : 26.048$ , whence  $x = 32.91$ . The temperature of the working room should be kept at about  $20^\circ$ , since the rotatory power of lactose diminishes in a small degree as the temperature rises. Double the quantity mentioned, *viz.*, 65.82 grams of milk are placed in a 100 cc. flask, clarified with mercuric nitrate solution, the volume completed to the mark, the contents of the flask well shaken, poured upon a filter, and the filtrate polarized in a 400 mm. tube. A similar quantity of the milk is placed in a 200 cc. flask and subjected to the same treatment. The polarimetric data obtained are used for calculating the true volume of liquid in the flask and the true percentage of lactose and the true volume occupied by the precipitate, in accordance with the rule already given, or with sufficient accuracy by Scheibler's formula. The acid mercuric nitrate solution is prepared as follows:

Dissolve mercury in double its weight of nitric acid, specific gravity 1.42, and add to the solution five volumes of water. This solution is more dilute than the one recommended in the original paper, it having been noticed that a stronger solution colors the precipitated proteid matter slightly yellow (xanthoproteic reaction). Ten cc. of the reagent are to be employed instead of two, as directed for the stronger solution. In preparing the solution of milk in the 200 cc. flask it may be necessary at times to use more than this quantity of the acid mercuric nitrate in order to secure a filtrate entirely free of turbidity.

An inspection of the data in the table shows a general agreement between the volume of the precipitate found and the percentage of fat in the sample with the exception of one instance, *viz.*, No. 11. It is evident that in solutions so dilute, a slight variation in the volume has a very small influence on the percentage of sugar found. An error of 0.05 degree in the reading of the dilute solution (200 cc. flask) makes an error of 0.05 per cent. in the result. The error due to one cc. of the precipitate in the dilute solution is approximately 0.05 per cent. It is therefore evident that with proper care the percentage of sugar can be determined to within one-tenth per cent. by the polarimetric method and this is entirely sufficient for all practical purposes.

## A STUDY OF THE ZIRCONATES.

BY F. P. VENABLE AND THOMAS CLARKE.

Received March 6, 1896.

THIS class of compounds of zirconium has received but little attention from chemists. The chief investigator in the past who has worked in this field was Hiortdahl.<sup>1</sup> Of recent years several papers by L. Ouvrard<sup>2</sup> have appeared. The accounts given in the various text books of these zirconates are based upon the work of Hiortdahl or upon such abstracts of it as were to be found in the *Jahresberichte*, or in such dictionaries as that of Watts. This is unfortunate, as to the best of our knowledge the work of Hiortdahl itself is in some respects inaccurate and erroneous, and the abstracts of it are misleading. Before giving an account of our own experiments, it may be well to gather together the statements regarding these bodies as given by Watt and in the original article of Hiortdahl.

Watts says that the compounds of zirconia with the stronger bases are obtained by precipitating a zirconium salt with potash or soda, also by igniting zirconia with an alkaline hydroxide. "Zirconate of potassium thus obtained, dissolves completely in water." His first mode of preparing the zirconates is very questionable; the last statement is not true. He then goes on and describes zirconates of sodium, calcium and magnesium, as described by Hiortdahl. The details of Hiortdahl's analyses, etc., will show on what an imperfect basis the knowledge of the constitution of these bodies rests. Hiortdahl states that he secured direct union only by ignition with alkaline carbonates. His attempts with the volatile chlorides failed. On heating zirconia with sodium carbonate one equivalent of carbon dioxide was driven out, and it is on the loss of carbon dioxide upon ignition that his figures for the composition of the resulting products are largely based. On heating equivalent amounts of zirconia and sodium carbonate a crystalline mass was obtained, which slowly absorbed moisture from the air. On treating this with water no decomposition was noted at first, but soon the water became alkaline and zirconia separated. This was taken as proof

<sup>1</sup> *Ann. Chem. Pharm.*, 137, 34, 236.

<sup>2</sup> *Compt. Rend.*, 112, 1444-46, and 113, 1021-22.

that the zirconia was decomposed by the water. In the experiment 0.3910 gram zirconia heated with 0.3130 gram sodium carbonate to a dark redness for nine hours lost 0.1310 gram carbon dioxide, and on treatment with water 0.3871 gram "zirconia," or 99.03 per cent. was left. If an excess of sodium carbonate is used one can drive out two equivalents of carbon dioxide. A little further down he notes that the "*Gewichtsverlust zugleich von der Temperatur und der Dauer des Glühens abhängt.*" These are the determinations from which formulas for the zirconates are worked out.

It is scarcely necessary to say that for purposes of calculation these figures are entirely worthless. The loss of carbon dioxide is due to a partial formation of hydroxide as well as to a combination with zirconia. The fused mass of sodium carbonate, hydroxide, zirconate and unchanged zirconia will of course prove hygroscopic, and water will wash away all except the last two mentioned. We have failed to get any positive evidence that a zirconate formed by fusion was decomposed by water or was appreciably soluble in it.

In his second paper, Hiortdahl treats the fused mass of zirconia and sodium carbonate with water acidified with hydrochloric acid and analyzes the residue, finding in it:  $\text{ZrO}_2$ , 78.54 per cent.;  $\text{Na}_2\text{O}$ , 5.40 per cent.; and  $\text{H}_2\text{O}$ , 16.89 per cent., corresponding to  $\text{Na}_2\text{O} \cdot 8\text{ZrO}_2$ . He gets the zirconate of magnesium and calcium by fusing zirconia and silica with magnesium chloride and calcium chloride respectively.

Ouvrard obtained his zirconates by fusions with the chlorides, also using those of lithium, calcium, strontium and barium. In some cases, instead of using zirconia, he took powdered zircons, obtaining silico-zirconates.

In our own experiments the following methods of forming the zirconates were tried:

- I. Fusing in boron trioxide, the zirconia and the basic oxide (Ebelmen).
- II. Fusing zirconia with alkaline carbonates, (Hiortdahl).
- III. Fusing zirconia with alkaline hydroxides.
- IV. Fusing zirconia with alkaline or earthy chlorides (Hiortdahl).

V. Precipitation of solutions of zirconium salts with alkaline hydroxides (Watts).

VI. Dissolving zirconium hydroxide in strong solutions of sodium or potassium hydroxide and precipitation by dilution or by neutralization with an acid.

#### I. FUSION WITH BORON TRIOXIDE.

This method, made use of by Ebelmen in the case of other oxides, is useless in the case of zirconia, because this oxide is not taken up by the boron trioxide, and so does not come in contact with the other oxide. The melt of boron trioxide was kept at a high temperature for a number of hours without any appreciable solvent action upon the zirconia, added in small portions.

#### II. FUSION OF ZIRCONIA WITH ALKALINE CARBONATES.

The purified zirconia used had been dried at the temperature of the steam bath and therefore was not in the inactive condition brought about by igniting it at a very high temperature. This was the case in the subsequent experiments also.

It is by fusion with sodium carbonate that Hiortdahl claimed to have prepared his ziconates. Ouvrard seems to have gotten little besides crystals of zirconia. Very little action could be seen in the experiments described below. The zirconia sank to the bottom of the fused mass and remained without apparent change for hours. Varying the time of heating did not seem to have much effect upon the results.

After the fused mass had cooled it was leached with successive portions of water until no alkali could be detected. The wash water contained no zirconium. As the mass left will absorb carbon dioxide, it was dried as rapidly as possible at about 150° to constant weight. Dilute hydrochloric acid was used to separate the zirconate formed from the unchanged zirconia. As this zirconia was now in the ignited and even crystalline form, it was concluded that it was insoluble in the dilute acid. The zirconia in the solution was precipitated as hydroxide and determined as oxide, and the alkali determined in the filtrate. Two grams of zirconia were used in each case and a large excess of the carbonate. The amount of unattacked zirconia ranged from ninety-



three to ninety-nine per cent., showing thus very little action after many hours of fusion. In some cases, therefore, the amount of supposed zirconate obtained was too small for reliable analysis.

#### I. WITH SODIUM CARBONATE.

Three experiments with sodium carbonate were carried to completion.

1. Two grams zirconia and eight grams sodium carbonate were fused three hours. Amount of residue after leaching, soluble in dilute hydrochloric acid, 0.1588 gram, or eight per cent. In this  $ZrO_2 = 75.70$  per cent.;  $Na_2O = 24.30$ .

2. Two grams zirconia fused with sixteen grams sodium carbonate for four hours. Amount of residue soluble in hydrochloric acid, 0.3042 grams. Percentages:  $ZrO_2$ , 74.18;  $Na_2O$ , 25.81. These correspond fairly with  $(ZrO_2)_2(Na_2O)_1$ .

3. Two grams zirconia fused with sixteen grams sodium carbonate for eight hours. Amount soluble in dilute hydrochloric acid 0.1220 gram, or six per cent. Percentages:  $ZrO_2$ , 58.16;  $Na_2O$ , 41.84.

#### II. WITH POTASSIUM CARBONATE.

When potassium carbonate was used the action was so slight that it was not possible to get enough for analysis. In one case, after heating for ten hours, the amount soluble was just one-half per cent. This accords with the observation of Ouvrard.

Of course it is possible that the leaching with water had a partially decomposing effect upon the zirconates. Very little could be justly concluded, however, from experiments in which there was so little action, therefore the effort at forming the zirconates by fusion with the carbonates was abandoned.

#### III. FUSION OF ZIRCONIA WITH HYDROXIDES.

##### 1. *Fusion with sodium hydroxide.*

Here considerable action was noticed. The fusions were made in a silver dish. The heating was kept up until the mass became semi-solid. The treatment of the fused mass and the analysis were carried out as before. No zirconium was detected in the wash water.

1. Two grams zirconia fused with eight grams sodium hydroxide. Total amount dissolved 1.1855 grams. An analysis, reduced to dry basis, gave  $\text{ZrO}_2$ , 92.29, and  $\text{Na}_2\text{O}$ , 7.65.

2. Same amount taken as in Experiment 1. Total amount dissolved 0.7655 gram, containing  $\text{ZrO}_2$ , 93.19, and  $\text{Na}_2\text{O}$ , 6.22.

3. Two grams zirconia and sixteen grams sodium hydroxide. Amount dissolved 0.8004 gram, containing  $\text{ZrO}_2$ , 92.57, and  $\text{Na}_2\text{O}$ , 7.38.

4. Two grams zirconia were fused with eight grams of sodium dioxide, instead of the hydroxide. Amount dissolved 0.7074 gram, and this contained 91.21 per cent.  $\text{ZrO}_2$ .

$\text{Na}_2\text{O} \cdot (\text{ZrO}_2)_2$  contains  $\text{ZrO}_2$ , 92.20; and  $\text{Na}_2\text{O}$ , 7.80.

$\text{Na}_2\text{O} \cdot (\text{ZrO}_2)_3$  contains  $\text{ZrO}_2$ , 93.29; and  $\text{Na}_2\text{O}$ , 6.76.

2. *Fusion with potassium hydroxide.*

These were carried out in a manner similar to those with sodium hydroxide and the action seemed to be about the same. In each experiment two grams of zirconia were taken and fused with sixteen grams of potassium hydroxide.

1. Dissolved by hydrochloric acid 0.8850 gram which contained 79.63 per cent.  $\text{ZrO}_2$ .

2. Dissolved 1.5241 grams which contained  $\text{ZrO}_2$ , 82.98;  $\text{K}_2\text{O}$ , 17.00.

3. Dissolved 1.2078 grams which contained  $\text{ZrO}_2$ , 78.59;  $\text{K}_2\text{O}$ , 21.40.

4. Dissolved 0.9297 gram which contained  $\text{ZrO}_2$ , 85.51;  $\text{K}_2\text{O}$ , 14.49.

In analyzing these alkaline zirconates the water present was not determined. The moist powder was treated with hydrochloric acid, the insoluble portion caught upon a filter, and the zirconia and alkali determined in the filtrate and the results calculated upon a dry basis. If the analysis given by Hiortdahl is calculated upon a dry basis, it gives for  $\text{ZrO}_2$ , 93.51, and  $\text{Na}_2\text{O}$ , 6.49, or very nearly the numbers gotten in Experiment 2 in the fusions with sodium hydroxide.

It is difficult to interpret the results of these fusions with the alkaline carbonates and hydroxides. The fusions do not yield the same definite results each time, and indeed it can not be claimed from the analyses that definite zirconates have been pre-

pared. Some allowance must be made for the imperfect method of separation of the zirconate from the unchanged zirconia, some of the former being taken up by prolonged digestion with hydrochloric acid. There is a marked tendency, however, toward the formation of certain zirconates under approximately the same conditions. Two of the experiments with sodium carbonate give results fairly in accordance with the formula  $(\text{Na}_2\text{O})(\text{ZrO}_2)$ . In the fusion with sodium hydroxide the results range from  $(\text{Na}_2\text{O})(\text{ZrO}_2)$ ,  $[\text{ZrO}_2 = 90.76; \text{Na}_2\text{O} = 9.24]$ , to  $(\text{Na}_2\text{O})(\text{ZrO}_2)$ ,  $[\text{ZrO}_2 = 94.08; \text{Na}_2\text{O} = 5.92]$ , and it is with these that the analysis of Hiortdahl agrees, though his was a fusion with sodium carbonate. Why there should be this difference is not very clear. The tendency is manifestly toward the formation of what may be called the polyzirconates, having a considerable excess of zirconic acid. In the case of potassium the carbonate failed to give a compound. The hydroxide gives results ranging from  $(\text{K}_2\text{O})(\text{ZrO}_2)$ ,  $[\text{ZrO}_2 = 79.57; \text{K}_2\text{O} = 20.43]$ , to  $(\text{ZrO}_2)(\text{K}_2\text{O})$ ,  $[\text{ZrO}_2 = 86.74; \text{K}_2\text{O} = 13.26]$ ; again polyzirconates with excess of zirconia.

Other fusions were carried out with sodium and potassium hydroxides, and the resulting masses were leached with dilute acetic acid, a solvent which had to be used in leaching away the alkaline earths in the subsequent experiments. In the case of sodium the leaching removed practically all of the alkali. In the case of potassium a substance containing  $\text{ZrO}_2$ , 78.59 per cent., and  $\text{K}_2\text{O}$ , 21.41 per cent. was left. This nearly corresponds to the formula  $\text{K}_2\text{O}(\text{ZrO}_2)_2$ . It is almost exactly the result gotten in one of the previous experiments.

3. Lithium gave no zirconate when the carbonate was used for the fusion. With the hydroxide it gave the following results:

Two grams  $\text{ZrO}_2$  were fused with excess of lithium hydroxide, leached with dilute acetic acid and with water. This gave on analysis  $\text{ZrO}_2$ , 89.11 per cent.;  $\text{Li}_2\text{O}$ , 10.99 per cent. Percentage of  $\text{ZrO}_2$ , calculated for  $\text{Li}_2\text{O} \cdot 2\text{ZrO}_2$ , is 89.13.

4. Calcium oxide was also heated for a number of hours with zirconia and gave the following results:

	I.	II.	Calculated for $\text{CaO} \cdot \text{ZrO}_2$
$\text{ZrO}_2$ .....	70.11	70.83	68.54
$\text{CaO}$ .....	29.88	29.14	31.46

These residues, after treatment with dilute acetic acid and water, were crystalline.

5. Barium hydroxide differs from that of calcium in that it fuses readily and thus affords much better opportunity for reaction. The fusion gave abundant evidence of action. The excess of hydroxide was washed out with water. The carbonate present was dissolved away with dilute acetic acid until there was no more barium in the wash water. No zirconia was found in any of these washings. Towards the latter part of the washing the solid particles settled out with great difficulty. The residue was analyzed with the following result :

	Found.	Calculated for $\text{BaO} \cdot \text{ZrO}_2$
$\text{ZrO}_2$ .....	55.51	55.95
$\text{BaO}$ .....	44.49	44.05

This is a grayish white powder, very fine and easily soluble in hydrochloric acid. Practically all of the zirconia was taken up, leaving little undissolved by the hydrochloric acid.

6. Strontium oxide was prepared by ignition of the nitrate and heated in the same way as the calcium oxide. This mass was pinkish white, probably from slight impurities, and was completely soluble in dilute hydrochloric acid. On analysis the following results were obtained :

	Found.	Calculated for $\text{SrO} \cdot \text{ZrO}_2$
$\text{ZrO}_2$ .....	54.22	54.55
$\text{SrO}$ .....	45.77	45.45

7. The magnesia (eight grams) and zirconia (two grams) was heated together for about four hours and then treated in the same manner as the calcium fusion, *i. e.*, first leached with dilute acetic acid and then washed with water until free from magnesia. The residue gave evidence of being crystalline.

	Found.	Calculated for $\text{MgO} \cdot \text{ZrO}_2$
$\text{ZrO}_2$ .....	76.28	75.30
$\text{MgO}$ .....	23.70	24.70

## IV. FUSION OF ZIRCONIA WITH CHLORIDES.

This method was used by Hiortdahl in preparing the zirconates of magnesium and calcium, and by Ouvrard for the same, and also for strontium, barium and lithium. According to the latter they all gave zirconates of the form  $M_2ZrO_4$ .

*1. Fusion with sodium chloride.*

There appeared to be very little action. The fusion was washed with water until free from chlorine. It was then treated as in the case of the carbonates. When two grams of zirconia were fused with sixteen grams of sodium chloride, it was found that less than two per cent. had been dissolved. In a second experiment, after heating six hours, the amount dissolved was less than two-tenths of a per cent.

*2. Fusion with potassium chloride.*

No action was observable. When two grams of zirconia were heated a number of hours with an excess of potassium chloride and the mass then treated as above, only three-tenths of a gram had been acted upon. There seemed to be even less action in the case of lithium chloride at the temperature attainable by means of an ordinary water-blast lamp.

*3. Fusion with alkaline earths.*

Two attempts were made to prepare magnesium zirconate by fusing zirconia with magnesium chloride and ammonium chloride. It was not possible to prevent decomposition of the magnesium chloride. There seemed to be some action, but much difficulty was experienced in separating the products. The method described by Ouvrard gave evidences of zirconium in the washings.

In the case of fusions with calcium chloride no action could be observed. Two experiments were made, following closely the directions of Ouvrard, except as to temperature possibly, as to which no exact directions were given. A water-blast lamp was used for several hours. After leaching and washing, the mass left behind gave no zirconium to hydrochloric acid.

Our experiments with the chlorides have led us to believe that there is little or no action between zirconia and the chlorides of the alkalis or alkaline earths except where these chlorides are

decomposed by the heat and oxides formed. Any action noticed is to be attributed to the oxides.

#### V. PRECIPITATION FROM THE SOLUTION OF A ZIRCONIUM SALT BY MEANS OF AN ALKALINE HYDROXIDE.

Watts speaks of this method but no experiments are recorded. It seemed to us upon examination of the question that very little evidence as to the existence of the zirconates or their properties could be drawn from such a method of preparation as this. It has been repeatedly observed that the precipitate formed by means of ammonium hydroxide is extremely hard to wash free from ammonia. After a very large number of washings, however, it is practically free from ammonia. The same is true of sodium and potassium hydroxides. Is it to be inferred that a definite zirconate is precipitated? At what point shall the washing be stopped, for manifestly some washing is necessary? Equally it cannot be decided because of this loss of alkali by prolonged washing, that we have a decomposition of the zirconate caused by the action of the water. It, therefore, seemed to be quite useless to make analyses of the precipitates gotten with different degrees of washing; especially as somewhat similar experiments were carried out under the next heading.

#### VI. THE SOLUTION OF ZIRCONIUM HYDROXIDE IN CAUSTIC ALKALI.

It was found that zirconium hydroxide was perceptibly soluble in solutions of potassium and sodium hydroxide. Experiments were first made with a view of determining the extent of this solubility. Solutions of the two alkalies were made up of different strengths, an excess of zirconium hydroxide added, and the solution then boiled. After cooling, a measured quantity of the solution was drawn off and the amount of zirconia present determined.

A 50 per cent solution potassium hydroxide dissolved per cc. 0.00233 gram.

33	"	"	"	"	"	"	"	0.00097	"
25	"	"	"	"	"	"	"	0.00075	"
12	"	"	"	"	"	"	"	0.00009	"

In the case of sodium hydroxide there seemed to be a stronger solvent action.

A 33 per cent solution dissolves per cc. 0.00245 gram.

25	"	"	"	"	"	"	0.0012	"
12	"	"	"	"	"	"	0.0005	"

If a concentrated solution of alkali, saturated with zirconium hydroxide, is diluted, a portion of the zirconium will be precipitated. Neutralization with acid will also cause a precipitation of the zirconium. In both cases alkali is retained by the precipitate in spite of washing. Analyses were made of some of these precipitates after very thorough washing (in no case was less than a liter of water used.) The results in four experiments were sufficient to show that these precipitates were practically zirconium hydroxide with a varying percentage of alkali, this percentage ranging from 1.15 to 3.94. It is possible to assume that zirconates were formed and then decomposed by the action of the water during the washing, but it seems more probable that this is, as is true in the case of so many hydroxides precipitated by alkaline hydroxides, merely a stubborn retention of alkali. Assuming that the strong alkaline solutions held zirconates in solution, attempts were next made to prepare other zirconates by precipitation from them.

The addition of solutions of various salts gave small precipitates which seemed to be formed mainly because of the dilution of the alkaline hydroxide and to consist almost entirely of zirconium hydroxide. It was necessary, therefore, to use strongly alkaline solutions of the compounds of the elements to be experimented with. This greatly diminished the choice of compounds. Concentrated solutions of aluminum and zinc hydroxides in potassium hydroxide gave precipitates but they were in too small amounts for reliable analyses to be made.

Summing up the results of the experiments performed, it is clear that the method yielding the best results for the preparation of the zirconates is fusion of gently dried zirconia with hydroxides or prolonged heating with the oxides. In the case of the alkaline earths this yields zirconates containing one equivalent of each oxide, as  $\text{CaO} \cdot \text{ZrO}$ , etc. The same is true of the magnesium compound. For lithium the compound obtained was  $\text{LiO} \cdot \text{ZrO}$ . For the alkalis it seemed to be possible to ob-

tain only zirconates having a largely preponderating proportion of zirconia. There seems to be a tendency toward the formation of distinct compounds under certain conditions. These polyzirconates, and the lithium compound also, may be decomposition products due to the action of the water used in leaching. No other mode of separation from the products of the fusion could be devised by us, however. If they are produced by the decomposing and solvent action of the water, it is a little strange that a point should be reached beyond which the leaching extracted no more alkali, and that this point varied with changed conditions. This is not the case where zirconium hydroxide has been precipitated by an alkali.

#### DOUBLE ZIRCONATES.

Two attempts at the formation of double zirconates were made.

##### 1. *Potassium calcium zirconate.*

About two grams each of zirconia, potassium hydroxide and lime were heated together for about four hours. There was evidence of considerable action. The mass was treated with dilute acetic acid and thoroughly washed. Then on treatment with dilute hydrochloric acid nearly the whole residue went into solution. The analysis gave  $\text{ZrO}_2$ , 67.21 per cent.;  $\text{CaO}$ , 31.06;  $\text{K}_2\text{O}$ , 1.11. This is a calcium zirconate,  $(\text{CaO}.\text{ZrO}_2)$ , with a small part of the  $\text{CaO}$  substituted by  $\text{K}_2\text{O}$ .

##### 2. *Potassium aluminum zirconate.*

Two grams of zirconia were fused for eight hours with two grams of potassium hydroxide and three grams of alumina. The mass was washed with dilute acetic acid until no more alumina was dissolved. The residue was treated with dilute hydrochloric acid and the insoluble portion removed by filtration. The analysis gave  $\text{ZrO}_2$ , 72.38 per cent.;  $\text{Al}_2\text{O}_3$ , 7.66;  $\text{K}_2\text{O}$ , 20.00. These experiments indicate the possible existence of double zirconates, and when time admits this point will be further examined.



## A MODIFIED AMMONIUM MOLYBDATE SOLUTION.

BY A. L. WINTON.

Received March 18, 1896.

WHEN phosphoric acid is determined by the molybdate method, it is a common practice to add fifteen grams of ammonium nitrate to the phosphate solution and heat before adding ammonium molybdate. By this means the separation of the yellow precipitate is greatly facilitated and the time of digestion shortened. But to dissolve this nitrate requires some time and very greatly reduces the temperature of the solution so that special care is necessary in heating it subsequently. In the laboratory of this station it has been our practice to simplify the process by omitting the separate addition of ammonium nitrate and using a molybdic solution containing the requisite quantity of the salt. Such a solution may be prepared according to the following formula :

I. Dissolve 1000 grams of molybdic acid in 4160 cc. of a mixture of one part of concentrated ammonia water (sp. gr. 0.90) and two of water.

II. Dissolve 5300 grams of ammonium nitrate in a mixture of 6250 cc. of concentrated nitric acid (sp. gr. 1.4) and 3090 cc. of water.

Add I to II slowly with constant stirring. Allow to stand for a few days in a warm place and decant off the clear liquid.

This solution has the same proportion of ammonium molybdate and free nitric acid as the molybdic solution of Fresenius, but differs from the latter in that *fifty cc. contain fifteen grams more of ammonium nitrate*. We have prepared the solution so as to contain this proportion of the salt because in the routine analysis of fertilizers in the station laboratory fifty cc. are most commonly employed. This quantity in our experience is usually sufficient for the precipitation of the soluble, insoluble or total phosphoric acid of mixed fertilizers in solutions representing four-tenths, two, and five-tenths grams respectively of the material.

In no case ought less than fifty cc. be used, for otherwise there may not be enough ammonium nitrate present for the perfect separation of the yellow precipitate. When a larger quan-

tity of molybdic solution is required, as, for example, in the determination of total phosphoric acid in ground bone, bone black, Thomas slag, etc., it may be added without fear that the larger quantity of ammonium nitrate contained in it will in any way interfere with the process. If, however, it is thought desirable, a special molybdic solution containing fifteen grams of added ammonium nitrate to every seventy-five or 100 cc. of the liquid may be prepared for such cases.

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### ON THE ESTIMATION OF SULPHUR IN PYRITES.

BY THOMAS S. GLADDING.

Received March 30, 1896.

IN the October (1895) number of this Journal, Dr. Lunge continues his discussion of the estimation of sulphur in pyrites. He presents no new experimental support of his position. He indirectly accuses me of having published a "private" communication without the sanction of the writer, Prof. Richards. In reply I will say that the words of Prof. Richards were published by myself, not only with full permission, but after a careful revision of the same by their author. Had Dr. Lunge addressed a note to Prof. Richards or to myself, he would have been saved from making a most unkind and needless accusation.

While Lunge attempts no further support of his position by chemical experiment, he makes the claim that any occlusion of barium chloride that occurs is compensated for by the solubility of barium sulphate in the acid liquor of precipitation. In his own words "my claim has been that my method by compensation of unavoidable errors, gives *correct results*."

I have investigated this claim of Lunge's, as far as it applies to the occlusion of barium chloride in his method, in the following manner: I have had one of our assistants repeat the work with chemically pure sulphate of ammonia, using two grams in each case, making comparison precipitations with a ten per cent. solution of barium chloride, the first by adding the barium chloride solution drop by drop from a burette, the second by sudden addition from a small beaker in which it had been brought to the boiling point. The results were as follows:

	By slow addition. Gram.	By sudden addition Gram.
Sulphur .....	0.4840	0.4880
Sulphur .....	0.4820	0.4873

These experiments show an occlusion of about 0.040 gram barium chloride and a corresponding error of 0.50 to 0.55 per cent. in the estimation of the sulphur present.

I repeated personally the second series of precipitations obtaining:

	Barium sulphate obtained. Grams.	Sulphur. Gram.
1 .....	3.5480	0.4878
2 .....	3.5430	0.4871

These experiments show an error of about 0.55 per cent. in the estimation of sulphur present. The greatest care was taken in washing these precipitates. Three washings by decantation, using seventy-five cc. of hot water each time, were followed by five washings on the filter paper.

I now fused these precipitates with chemically pure sodium carbonate, dissolved the flux in water, filtered from barium carbonate, acidified the filtrate with nitric acid, added silver nitrate and from the silver chloride obtained, calculated the equivalent of barium chloride. I obtained in one case 0.0552 gram silver chloride, corresponding to 0.040 gram barium chloride, in the other 0.0500 gram silver chloride, equivalent to 0.0364 gram barium chloride. Deducting these figures, we have:

BaSO <sub>4</sub> .....	3.5480	3.5430
BaCl <sub>2</sub> .....	0.0400	0.0364
Pure BaSO <sub>4</sub> obtained .....	3.5080	3.5066

The sulphur obtained from these corrected results are 0.4823 gram and 0.4821 gram. These corrected results agree very closely with those obtained by our assistant when using the dropping method. I now fused one of the precipitates obtained by the dropping method with sodium carbonate in the same way and obtained 0.0027 gram silver chloride, equivalent to 0.002 gram barium chloride. This shows that the occlusion of barium chloride is practically avoided by adding the barium chloride drop by drop, as 0.002 gram barium chloride would cause an error of only 0.026 per cent. in sulphur.

I now took up the question of the solubility of barium sulphate in the acid liquor of precipitation, imitating the conditions under which the actual analysis of pyrites is made. To 400 cc. water were added fifteen cc. strong ammonia. Hydrochloric acid was now added to acidify. To two such preparations I added 0.020 gram and 0.040 gram chemically pure ammonium sulphate, respectively. The solutions were brought to the boiling point and ten cc. barium chloride added. The liquid was boiled till clear and allowed to settle. I obtained :

	Barium sulphate. Gram.	Sulphur obtained. Gram.	Sulphur present. Gram.
1.....	0.034	0.00468	0.00484
2.....	0.069	0.00949	0.00969

The sulphur lost by the solubility of the barium sulphate in the acid solution in the above experiments amounts to 0.016 and 0.020 per cent. respectively.

The above work demonstrates conclusively that the method employed by Lunge of adding the barium chloride all at once causes an error of about five-tenths per cent. in the percentage of sulphur, and that such error is *not* compensated for by the solubility of barium sulphate in the liquor of precipitation, as such solubility is very slight, causing an error of less than 0.03 per cent.

In his first reply (March, 1895), Dr. Lunge objected to my method of estimating the 0.20 to 0.40 per cent. of sulphur, (that may be left in the ferric hydroxide), by the simple process of dissolving the latter in dilute hot hydrochloric acid, adding ten cc. of barium sulphate solution and letting stand over night. This he declared was wrong, owing to the solubility of barium sulphate in such solution. I showed by a few simple and rigid experiments that I was entirely right. These experiments were very easily capable of repetition. But Lunge did not choose to repeat them. The above experiments showing that the sudden addition of barium chloride will cause an error of several tenths of a per cent. are likewise very easily repeated and the separation of the occluded barium chloride as described, is so positive as to the error caused by Lunge's method of procedure, that I hope for a further answer from Dr. Lunge. On account

of the commercial importance of an accurate estimation of sulphur in pyrites, I have no doubt that a prompt repetition of my work as described above will soon be published by some other analyst, and the main point at issue, namely, the necessity of a very slow addition of the barium chloride solution, be settled.

### FURTHER NOTES UPON THE FATS CONTAINED IN THE TUBERCULOSIS BACILLI.

BY H. A. DE SCHWEINITZ AND MARION DORSET.

Received March 28, 1896.

IN the *Journal of the American Chemical Society*, for August, 1895, we published an article upon the composition of the tuberculosis and glanders bacilli, and noted the probable composition of the fats which are present in these germs in considerable proportion. The amount of crude fat in the tuberculosis bacilli is very large, having been found by us to be in round numbers thirty-seven per cent. of the weight of the dried germs. In the article referred to the amount of fat at our disposal was very small, and we could at that time determine only palmitic acid, and a high melting acid, which we stated appeared to be arachidic so far as the quantity at hand could be utilized. Recently we have made some further study upon these fats, and the results so far obtained seem to be of sufficient interest to warrant publication as a continuation of our previous work.

The quantity of crude fat available, which had been extracted from the germs was about three and five-tenths grams, and this was examined in the following way: It was first saponified in a closed flask with sodium hydroxide, in accordance with the method prescribed, for the determination of fats by the American Association of Official Agricultural Chemists, as this method seemed to give the most satisfactory results. The saponification yielded a hard soap which was difficultly soluble in water. The dissolved soap was acidified with sulphuric acid and submitted to distillation until 100 cc. of the distillate had been obtained, again in accordance with the usually prescribed method. The distillate had a pungent odor, something like that of sweet almonds, and when titrated with tenth normal hydroxide

solution, required for neutralization two and four-tenths cc. of the latter. The total amount of volatile fatty acid was therefore exceedingly small. As the total amount of sodium hydroxide required to neutralize the volatile acid from three and five-tenths grams fat was only 0.0096 gram, the total quantity of volatile acid could probably not have been 0.05 gram, an amount too small to permit of a determination of its character.

The non-volatile fatty acids which formed a hard layer in the distilling flask were filtered off and well washed with water to remove all sulphuric acids and salts. The mixture was partially soluble in cold ninety-five per cent. alcohol, but readily soluble in hot absolute alcohol. The only method that appeared practical for the separation of the fatty acids in this mixture, was a fractional crystallization. Even this was extremely troublesome, but finally by repeated efforts the larger portion of the acid was found to have a melting-point of  $62^{\circ}$  C., which remained constant upon recrystallization. The principal fatty acid was therefore palmitic. After the palmitic acid had been removed a residue remained which was partially soluble in cold eighty-five per cent. alcohol, and partially in hot eighty-five per cent. alcohol. The acid soluble in hot eighty-five per cent. alcohol after the first crystallization melted at  $85^{\circ}$  C., while two subsequent crystallizations raised the melting point to  $102^{\circ}$  C. Unfortunately again the quantity of this high melting acid was too small for further crystallization or identification. It was evidently the same acid that in our first article we noted as probably arachidic acid.

The acid soluble in cold eighty-five per cent. alcohol was further purified and gave white crystals that melted at  $42^{\circ}$ - $43^{\circ}$  C., which would correspond to lauric acid. The amount was too small to permit of a positive identification.

This examination of the tuberculosis fats has shown that it is principally a glyceride of palmitic acid. In addition there is a minute amount of the glyceride of a volatile fatty acid to which the tuberculosis cultures owe their characteristic odor, and very small amounts of probably lauric acid and an unusually high melting acid, an acid apparently with a larger carbon content, so far as we can find, than any before noted in plants.

We propose still to identify the volatile and non-volatile acids found in such small quantities, but as it will require probably several years to collect the material for this work, it has seemed best to give the results so far obtained at the present time.

### THE CASSEL-HINMAN GOLD AND BROMINE PROCESS.

BY PARKER C. MCILHINEY.

Received March 24, 1896.

THIS process, recently introduced by the Gold & Bromine Co., is for the extraction of gold from low grade ores, and those which will not give up their gold to amalgamation. If an ore is free milling no process yet devised can compete with amalgamation for its treatment, and if it is of sufficiently high grade to bear transportation and smelting charges, and contains nothing to interfere with the process of smelting, there is comparatively little inducement to use a wet process. But for ores such as the telluride ores of Colorado, which will not amalgamate, and in which the gold and tellurium compounds are of such a friable nature that they cannot be concentrated, and which are in addition of too low grade to smelt, some wet process must be used. The wet processes which have proved commercially successful are chlorination and the cyanide process. Of the cyanide process nothing need be said except that on many ores it has been used very successfully and from many others it fails to extract a sufficiently high percentage of the gold present. Chlorination has, after being the subject of a great deal of experimenting, been reduced practically to two methods of operation: the vat process, in which the ore is treated with chlorine gas and water, without agitation, and the Thies barrel process, in which the ore is agitated in a revolving barrel with water, bleaching powder, and oil of vitrol. Of the two the barrel process is more generally applicable as the ore cannot be leached in vats unless it is comparatively free from slime and allows the liquid to pass through it readily. The barrel process is recognized generally as better practice. It is evident that in the vat process the strongest solution of chlorine which can at any time be in contact with the ore will be an aqueous solution saturated at the ordinary temperature and pressure, because it

is impracticable to place the vats under pressure. In the barrel process it has also been found impracticable, on account of mechanical difficulties, to treat the ore with chlorine under any considerable pressure, and, therefore, in the Thies process the strength of the chlorine solution is almost as limited as in the vat process, and moreover it has been found impracticable to introduce the chlorine in the Thies process as free chlorine, and it is now made entirely by means of bleaching powder and oil of vitriol, introduced with the ore. In order to effect the solution of the gold in the ore in a reasonably short time it is not sufficient to introduce a *small* excess of chlorine but a very large excess must be used to so hasten the solution as to bring the time within permissible limits. This excess of chlorine goes to waste, and although very many attempts have been made to recover it, none have ever proved practicable. The only safe way to get the gold out is to use as large an excess of chlorine as possible, and as the solubility of chlorine in water prevents the use of more than a small amount, it sometimes happens, even with careful working, that the ore being improperly roasted no gold is obtained at all.

As a substitute for chlorine, bromine has been used by many experimenters, and its use has been attempted in mills by a simple substitution of bromine for chlorine. But as bromine is very expensive its use without recovery has not been successful.

The properties of the two halogens, as far as concerns their use on ores, are about as follows :

Bromine is, at ordinary temperature, a liquid, boiling at  $63^{\circ}$  C., and which may be easily liquified again by a condenser supplied with cold water.

Chlorine is a gas which must, according to Nieman,<sup>1</sup> be placed under a pressure of six atmospheres at  $0^{\circ}$  C. in order to liquefy it, or cooled to  $-35^{\circ}$  C. to condense it without pressure.

Bromine is soluble in water at  $15^{\circ}$  C. to the extent of three and two tenths per cent; this means about 25.5 pounds in 100 gallons of water.

Chlorine is soluble in water to the extent of about 0.76 per

<sup>1</sup> Brandes Arch., 36, 18; Dammer, Handb. Anorg. Chem., 1, 474.



cent. at 15° C.; this means about six pounds in 100 gallons of water.

Bromine is a much less powerful oxidizing agent than chlorine, and, as a result of this fact, oxidizable materials such as pyrites are much less acted upon by bromine than by chlorine. In fact it is possible to treat with bromine water pyrites containing gold and extract most of the gold as bromide without attacking much pyrites, which it is not possible to do with chlorine water.

Bromine dissolves gold more easily than chlorine. The experiments made by T. K. Rose, at the Royal Mint in England, recorded in his "Metallurgy of Gold," page 242, show that a saturated solution of chlorine in water, that is about 0.76 per cent. of chlorine, dissolved 57.6 parts of gold, while a two-tenths per cent. solution of bromine in water, less than one-third the strength of the chlorine, dissolved under exactly similar circumstances, 58.1 parts of gold.

These facts will render it very evident that if some means can be devised for recovering the bromine which has been used in the treatment of the ore much better results can be obtained than can be obtained by chlorination. Several plans have been devised for accomplishing this result, but only one has as yet been put into practical working in a mill. It consists in adding to the liquor which has acted upon the ore, and which stills contains a large excess of bromine as well as some bromides, sufficient chlorine or oxidizing agent and acid to liberate the bromine from the bromides and then to distil off the bromine by steam. The amount of liquid which it is necessary to distil off in order to free an aqueous solution of bromine from its bromine is surprisingly small. Using a solution of about fifteen pounds in 100 gallons the bromine is practically gone when about five per cent. of the liquid has distilled over. The liquid thus freed from bromine is in an ideal condition for the precipitation of gold, and this may be accomplished by any convenient method. It will then be seen that the process is in the main identical with chlorination as far as apparatus is concerned, except that to the liquid an addition of chemicals is made and

it is then heated up by steam and a small portion distilled off before precipitation.

The necessary steps may be stated as follows :

1. Crushing the ore preferably in a Blake crusher.
2. Drying.
3. Reducing to twenty to thirty mesh preferably by rolls.
4. Roasting, unless it is already almost completely oxidized.
5. Treating with bromine solution, preferably by agitation in a barrel, under some circumstances also by percolation in vats.
6. Drawing off the liquor and washing the ore with weak wash water from a previous operation, and after that either with water, or else with liquor from which the gold has been precipitated in a previous operation.
7. Adding to the strong liquor from leaching the ore sufficient chlorine, bleaching powder and acid, potassium permanganate and acid, or some other oxidizing agent, in sufficient quantity to liberate the bromine present as bromides.
8. Distilling off the bromine by steam.
9. Precipitating the gold.

With regard to the reduction of the ore to a proper fineness nothing need be said. It should be done exactly as if the ore were to be treated by chlorination.

The roasting, however, need not with ores which lose gold on roasting be carried so far as if the ore were to be chlorinated. The reasons why this is true are evident from a consideration of what has been said with regard to the differences in properties between chlorine and bromine; the less powerful oxidizing action of the bromine, the greater solvent power on the gold, and above all the possibility of making a strong solution of bromine, while in chlorination the solution is weak, render it possible to stop the roasting at a very much less perfect degree. The advantages of this will be apparent when the losses in gold, which occur during the last stages of roasting, are taken into account,<sup>1</sup> losses which result both from the volatility of the gold itself, and also from the fine particles being carried away by the current of air in the furnace. In roasting tellurides especially the losses in gold are enormous if the roasting is carried

<sup>1</sup> Rose, Metallurgy of Gold, p. 222.

too far. Küstel records the loss of twenty per cent. of the gold present during the oxidizing roasting of certain tellurides of gold and silver, and states that it is not a mechanical loss, but is due to volatilization. Rose records many other results which place beyond doubt the great advantage of restricting the roasting as much as possible. This loss of gold toward the end of the roasting causes one of the greatest difficulties in chlorination. Since one per cent. of sulphur requires 200 pounds of chlorine per ton of ore, the loss must be borne because it is necessary to carry on the roasting to a high degree, otherwise no gold at all, or only a part, will be obtained.

The mechanical treatment of the ore during the action of the bromine upon it is not different in any material way from the treatment with chlorine; the ore is charged into the barrel in the same way. The bromine solution is added at the bottom, through the pipe which serves to draw it off again after the treatment. If the percolation process in vats is used the bromine solution is introduced into a covered vat, using the same precautions to avoid packing of the ore, etc., that are now used in the vat process for chlorination, and in the cyanide process.

After the ore has been acted upon by the bromine solution for a sufficient length of time the liquor is drawn off at the bottom and weak wash water from a previous operation introduced at the top of the ore, the first liquor, which is strong, being sent to a strong liquor tank, and the subsequent weaker liquor being reserved in a weaker liquor tank for subsequent use in leaching ore. From the strong liquor tank the solution runs into a still. One form of apparatus which has been used successfully, but which is now being superseded by an improved form consists of a covered stone tank heated by live steam, and provided with an outlet for the vapors, which leads to a stoneware condenser. Into the condenser, weak liquor from the weak liquor tank is allowed to enter with the vapors and in this way a bromine solution of the proper strength to run into the barrel with more ore is obtained. To the liquid in the still, before steam is turned on, bleaching powder and oil of vitrol, or

potassium permanganate and oil of vitrol, is introduced in sufficient quantity to free the bromine present as bromides. The chemicals used for this purpose in the mill have been bleaching powder and oil of vitriol. It may be asked why, if bleaching powder and acid are to be used to liberate the bromine from bromide, it would not be just as well to treat the ore with them in the first instance; to this it may be answered that in the process only as much chlorine is used as will liberate the amount of bromine which has actually combined with the ore, whereas in chlorination an excess is used which amounts to several times this amount. After the bromine is out of the liquid in the still it is run hot into the precipitating tanks, where it may be precipitated in any desired way. The only difference between the precipitation here and in chlorination is that here there is no troublesome excess of chlorine to be disposed of by sulphur dioxide or to use up large quantities of precipitants. The precipitant actually used in the mill has been powdered sulphide of iron, which in the hot liquor precipitates the gold quickly and completely. The gold is caught in a filter press and refined as usual.

Where ores are to be treated, in which the gold is present partly in too large pieces to dissolve rapidly in the bromine solution, the washed ore must be allowed to run over amalgamated plates, and as the gold is in perfect condition to amalgamate, it is easily caught.

The details of the process have been worked out by the Nellie Bly Gold Mining & Reduction Co., in Magnolia, Colorado, using an ore which has never before been successfully treated. It is a siliceous ore containing from \$8.00 to \$20.00 in gold per ton as tellurium compounds and nothing else of value. It cannot be amalgamated, concentrated, treated by the cyanide process, nor shipped to the smelters in Denver at a profit, and consequently presents a very difficult problem which has, however, been solved with entire success.

The process is also about to be introduced in other localities, and it seems entirely probable that it may in the near future displace chlorination to a great extent, at least.

## A SIMPLE METHOD FOR DETERMINING THE NEUTRALITY OF THE AMMONIUM CITRATE SOLUTION USED IN THE ANALYSIS OF FERTILIZERS.

BY N. W. LORD.

Received April 6, 1896.

It is well known that the preparation of a strictly neutral solution of ammonium citrate requires considerable judgment, owing to the uncertainty of the color change when using ordinary indicators in the presence of salts of citric acid.

Even when using corallin, as directed in the official methods of the Association of Official Agricultural Chemists, some uncertainty remains. "Huston's Method" with alcoholic solutions of calcium chloride, while very exact, is a little troublesome.

The following method has been in use in my laboratory for over a year and has proved rapid and exact. I have used it only with litmus as the indicator as the tint so obtained is very easily matched, probably corallin or cochineal would do as well.

The method consists in establishing an accurately neutral color for comparison, by superimposing two tubes, one containing acid litmus, and the other alkaline litmus, and looking through both at once. Then comparing this with the diluted citrate solution, colored to the same depth with the same amount of litmus tincture. The details are as follows:

Add pure litmus solution to about 200 cc. of neutral distilled water until it is colored distinctly, but not deeply. Take half of this and dilute further with its own volume of water. Now take three clear fifty cc. "Nessler tubes," fill two of them with the diluted liquid, and the third to the same depth with the stronger solution. To one of the two first add a drop of dilute sulphuric acid, to the other a drop of ammonia. Set these tubes one in front of the other, so that the light passes through both, thus giving a strictly neutral purple color; a little care will enable one to see them almost like one tube against a sheet of white paper in a ground glass. It makes no difference which tube is in front. Now to the liquid in the third tube containing the stronger solution (which is obviously equal in color depth to the double thickness of the first two tubes), add five cc. of the citrate solution to be tested, and compare the color

produced with the color shown by the doubled tubes. The slightest acidity or alkalinity of the citrate is at once shown by difference of tint; the test is very sensitive. The amount of acid or alkali needed to bring it right, can then be easily obtained by adding one-half normal sulphuric acid or ammonia; then by calculating to the five cc. taken, the necessary addition to the "stock" solution can be found and when made the solution re-tested with remainder of the colored water. The operation is very rapidly performed and the results surprisingly exact. Solutions so neutralized, when tested by Huston's method, have always been found exactly correct. The litmus solution should be prepared from the alcohol extracted litmus, as directed by Sutton.

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### THE COPPER ASSAY BY THE IODIDE METHOD.

BY ALBERT H. LOW.

Received March 23, 1896.

THE last edition of Dr. Peters' Modern Copper Smelting contains a description of the writer's modification of the copper assay by the iodide method. The following description of the same method embodies whatever changes have been deemed desirable up to date as the result of almost daily work upon copper ores and products. For the most accurate technical work I prefer it to all other methods. For practical work it exceeds the electrolytic method in accuracy, notwithstanding that the latter, when every precaution is taken, is perhaps theoretically more accurate.

#### COPPER ASSAY BY THE IODIDE METHOD.

Prepare a solution of sodium hyposulphite containing about nineteen grams of the pure crystals to the liter. Standardize as follows: Weigh accurately about 0.200 gram of pure copper foil and place in a flask of about 250 cc. capacity. Add five cc. of a mixture of equal volumes of strong nitric acid (1.42 sp. gr.) and water, and thoroughly boil off the red fumes,—a very essential point. Now remove from the lamp and add six to seven grams of crystallized zinc acetate, roughly weighed, and about fifteen cc. of water. Instead of adding the zinc acetate in this way, a cold saturated solution may be kept on hand and about twenty

cc. taken, the additional fifteen cc. of water being then unnecessary. Heat to boiling for a moment and then cool to ordinary temperature, and dilute to a bulk of about fifty cc. Now add about three grams of potassium iodide and shake it about gently until dissolved. Cuprous iodide will be precipitated and iodine liberated according to the following reaction:  $2(\text{Cu} \cdot 2\text{C}_2\text{H}_3\text{O}_2) + 4\text{KI} = \text{Cu}_2\text{I}_2 + 4(\text{K} \cdot \text{C}_2\text{H}_3\text{O}_2) + 2\text{I}$ . The free iodine colors the mixture brown. Titrate at once with the hyposulphite solution until the brown tinge has become weak and then add sufficient starch liquor to produce a marked blue coloration. Now continue the titration cautiously until the blue tinge has entirely vanished. When almost at the end allow a little time after the addition of each drop to avoid passing the point. One cc. of the hyposulphite solution will be found to correspond to about 0.005 gram of copper. In the assaying of ores, etc., when half a gram is taken, one cc. of the standard hyposulphite would then equal about one per cent. copper. The reaction between the hyposulphite and the iodine is:  $2(\text{Na}_2\text{S}_2\text{O}_3) + 2\text{I} = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$ . Sodium iodide and tetrathionate are formed. The starch liquor may be made by boiling about half a gram of starch with a little water and diluting with hot water to about 250 cc. It should be used cold and must be prepared frequently for regular work, as it does not keep very well. The hyposulphite solution made of the pure crystals and distilled water appears to be very stable, showing no appreciable variation at the end of a month, when kept under reasonable conditions.

#### TREATMENT OF ORES.

Treat half a gram of the ore in a flask of 250 cc. capacity with five or six cc. of strong nitric acid and boil gently nearly to dryness. Then add five cc. of strong hydrochloric acid and again boil. As soon as the incrustated matter has dissolved add five cc. of strong sulphuric acid and heat strongly, best by manipulating the flask in a holder over a small naked flame, until the more volatile acids are expelled and the fumes of the sulphuric acid are coming off freely. Allow to cool and then add twenty cc. of cold water and heat the mixture to boiling to thoroughly dissolve any anhydrous sulphates of iron, etc. Now

filter to remove more especially any lead sulphate and receive the filtrate in a beaker about two and one-half inches in diameter. Wash the flask and filter with hot water and endeavor to keep the volume of the filtrate down to about fifty or sixty cc. Place in the beaker two pieces of sheet aluminum, which, for the sake of convenience in subsequent washing, may be prepared as follows: Stout sheet aluminum, say about one-sixteenth of an inch in thickness, is cut into pieces an inch and a half square, and then the four corners are bent, for about a quarter of an inch, alternately up and down at right angles. This scheme prevents the pieces from lying flat against each other or upon the bottom of the beaker, and their washing is thus facilitated. The same pieces of aluminum may be used repeatedly, as they are but little attacked each time. Add five cc. of strong sulphuric acid, cover the beaker and heat to boiling. Boil strongly for about seven minutes. Unless the bulk of the solution is excessive this will be quite sufficient with all percentages of copper. Ordinarily the aluminum will be found to be clean and nearly or quite free from precipitated copper. If, by chance, the copper adheres to any considerable extent, it will usually become loosened by a little additional boiling, or it may be removed by the aid of a glass rod. Transfer the solution back to the original flask, and, by means of a wash bottle of hot water, rinse in also as much of the copper as possible, leaving the aluminum behind. Drain the beaker as completely as possible and temporarily set it aside with the aluminum which may still retain a little copper. Allow the copper in the flask to settle and then decant the liquid through a filter. Again wash the copper similarly two or three times with a little hot water, retaining it as completely as possible in the flask. Finally wash the filter once or twice and endeavor to rinse all metallic particles down into the point. Now pour upon the aluminum in the beaker five cc. of a mixture of equal volumes of strong nitric acid (1.42 sp. gr.) and water and warm the beaker gently, but do not heat to boiling, as the aluminum would be thereby unnecessarily attacked. See that any copper present is dissolved and pour the warm solution through the filter last used, thus dissolving any contained particles of copper, and receive the filtrate in the flask containing the main



portion of the copper. At this stage do not wash either the aluminum or the filter, but simply remove the flask and set the beaker in its place. Heat the mixture in the flask to boiling and see that all the copper is dissolved. Then add about half a gram of potassium chlorate and again boil for a moment. This is to oxidize any arsenic present to arsenic acid and is a very important point. Remove the flask from the lamp and again place it under the funnel and wash the beaker, aluminum and filter with as little hot water as possible. Again boil sufficiently to remove every trace of red fumes. All the copper is now in the flask as nitrate. Add the zinc acetate and proceed from this point precisely as described with the original nitrate of copper solution in the standardization of the hyposulphite, finally calculating the percentage of copper present from the amount of standard hyposulphite required. One point, however, remains to be further explained. According to the equation previously given, half a gram of pure copper requires 2.62 grams of potassium iodide. While direct experiment shows this to be apparently true, yet it is found that with small percentages of copper, the reaction, when only the theoretical amount of potassium iodide is taken, is slow and in fact does not appear to proceed to completion until during the titration, which is thereby unduly prolonged. It is therefore best to use not less than three grams of potassium iodide in any case. An excess does no harm. Silver does not interfere with the method. Lead and bismuth are without effect, except that by forming yellowish iodides they may mask the end-point before adding starch. Lead is practically removed as sulphate at a previous stage. If bismuth is suspected in any appreciable amount, simply add the starch earlier in the titration. Arsenic when oxidized as described has no influence. The return of the blue tinge in the liquid by long standing after titration is of no significance, but a quick return of the color, which an additional drop or two of the hyposulphite does not permanently destroy, may indicate either an incomplete combination of all the nitric acid with zinc, or a failure to completely boil off the red fumes when dissolving the copper in nitric acid. The assay in such a case is spoiled. This trouble may be avoided by carefully following the directions

given and not guessing at strengths or quantities. The amount of zinc acetate recommended is a safe excess. Sodium acetate does not appear to work as satisfactorily.

For the assay of alloys, etc., the necessary modifications of the foregoing scheme are obvious.

The foregoing scheme directs the use of five cc. of dilute nitric acid for dissolving the copper previous to titration and prescribes six to seven grams, or about twenty cc. of a saturated solution of zinc acetate as a safe excess of neutralizing agent. It is obvious that if most of the nitric acid be boiled away the amount of zinc salt necessary is greatly reduced. In such a case, however, it is perhaps best, for safety's sake, not to use less than one-half the prescribed quantity. Half the zinc salt may thus be saved at the expense of a little more time. This is the ordinary practice in my own laboratory.

DENVER, COLORADO.

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## ON TWO SOURCES OF ERROR IN SUGAR HOUSE ANALYSES.

BY EDMUND C. SHOREY.

Received March 10, 1896.

INCIDENTAL to the study of the action of water of different temperatures on bagasse, I have had occasion to make some determinations which throw some light on a source of error in fiber determinations.

Finely cut cane was washed with cold water until the polariscope reading in a twenty cm. tube was 0; the excess of water squeezed out in a press, and three portions of fifty grams each taken. In one the moisture was determined by drying to constant weight in an air bath at 105° C.; the two others were treated with boiling water; one for five minutes and the other for two hours. The quantity of water used was in each case just sufficient to cover the cane chips, and at the expiration of the time the water and the chips were poured on a filter and washed four times with cold water, using each time the same quantity of wash water as was used in the original treatment. The filtrate so obtained was evaporated to dryness over a water-bath, dried at 105° C., and calculated to percentage of dry sub-

stance left after the exhaustion of sucrose with cold water. The filtrates obtained were decidedly milky, and this no amount of filtering would remove. A portion of filtrate on standing undisturbed for six days had *not* become less milky, and had thrown down *no* deposit.

The cane was prepared by cutting to fineness of saw dust in a meat chopper, and determinations have in all cases been made in duplicate.

The mean of six fairly mean concordant determinations is as follows :

(1) Treatment for five minutes with boiling water extracted seven and two-tenths per cent. of dry substance.

(2). Treatment for two hours with boiling water extracted twelve per cent. of dry substance.

To show the amount of error likely to result from using varying quantities of water and varying the time of boiling ; suppose that the fiber and dry substance from the treatment with cold water was ten per cent. of cane, we would have :

	Per cent.
Fiber extraction with cold water.....	10.0
" " " hot water five hours.....	9.3
" " " " " two hours.....	8.8

Dr. Beeson, of Audubon Park Sugar School, has pointed out in this Journal the errors in fiber determinations likely to result from the varying amounts of fiber in different parts of the same stalk of cane. This can be overcome, I think, by taking a sufficiently large sample and reducing it to a very fine state of division; but if fiber determinations by different chemists are to be comparable, some uniform method must be agreed upon. This method should provide for the fineness of division of cane or bagasse, the quantity of sample to be taken, the quantity of water to be used, the number of times washing, and the length of time of boiling.

In calculating the extraction by formulas similar to those given by M. Trubek in this Journal (Dec., 1895), I prefer to dry the residue from alcoholic extraction and call this fiber. The object being simply to compare the fiber in the cane with that in the

bagasse, and this method I find gives more uniform results with a minimum of labor:

A second source of error in sugar house analyses to which I wish to draw attention is in the determination of albuminoid nitrogen as commonly carried out.

In the official method for albuminoid nitrogen in finding stuffs the directions are to heat to boiling, add cupric hydrate, filter when cold and wash with cold water. In the determinations of albuminoid nitrogen in cane juice made by W. Maxwell, and published by him in a Bulletin of Louisiana Experiment Station, this method was modified, but for what reason I am unable to say. According to this modified method the juice was heated to boiling, cupric hydroxide added, boiled ten minutes, filtered hot and washed with hot water. Both these methods introduce a serious error, owing to the fact that when cane juice in its natural acid condition is heated a change is brought about in the albuminoid nitrogen contained therein, and in consequence the amount of albuminoids as determined by either of these methods is not really that which is in the juice in the plant, but that which is left from the action of heat and the acid in the juice.

During the past two years I have made a large number of determinations, as follows: I. Total nitrogen in juice; II. Albuminoid nitrogen in cold juice; III. Albuminoid nitrogen in juice which had been heated to  $71^{\circ}$ – $72^{\circ}$  C.; IV. Albuminoid nitrogen in juice which had been boiled one minute. For total nitrogen the Gunning method was used, and for albuminoids cupric hydroxide was added to cold juice, filtered cold and washed with cold water, the precipitate and filter paper treated by Gunning method. In each case twenty cc. of juice have been used, and the results calculated to percentage of total solids as given by Brix spindle; the difference between total nitrogen and albuminoids has been called amides and calculated to asparagins.

As the results have been the same in all cases, I give below two analyses which I have already communicated to the Planter's Monthly, (Honolulu).

1. Brix, 17.3 ; Purity, 91.

Acidity, 100 cc. juice = ten cc.  $\frac{N}{10}$  alkali.

Total nitrogen 1.115 per cent. of total solids.

	Per cent. of nitrogen compounds.	
	Albuminoids.	Amines.
Cold juice.....	95.5	4.5
Juice heated 71°-72° C.....	87.5	12.5
Juice boiled one minute.....	86.7	13.3

2. Brix, 18.2 ; Purity, 90.9.

Acidity, 100 cc. juice = 11.3 cc.  $\frac{N}{10}$  alkali.

Total nitrogen 1.032 per cent. of total solids.

	Per cent. of nitrogen compounds.	
	Albuminoids.	Amines.
Cold juice.....	93.5	6.5
Juice heated 71°-72° C.....	81.4	18.6
Juice boiled one minute.....	77.4	22.6

Although I have in these analyses designated the body or bodies formed from the albuminoids by heat amines, I am of the opinion for several reasons that they are peptones or soluble albuminoids. I am at present investigating the matter. Whatever they are, the fact remains that the albuminoid nitrogen determinations on cane juice as carried out by any method which calls for the heating of the raw acid juice are not reliable.

LABORATORY KOHALA SUGAR Co.,  
KOHALA. HAWAII.

## REVIEW.

### BERTHELOT'S CONTRIBUTIONS TO THE HISTORY OF CHEMISTRY.<sup>1</sup>

Marcellin Berthelot, Professor of Chemistry in the Collège de France, Perpetual Secretary of the Academy of Sciences, Senator, Minister of Public Instruction, and recently appointed Minister of Foreign Affairs, known to the scientific world by his masterly researches in synthetical chemistry, has added to these honors that of editing the most important and far-reaching documents pertaining to the history of chemistry ever brought to light.

The six handsome quarto volumes published by him between the years 1887 and 1893, contain the most ancient Greek, Arabic, Syriac, and Latin treatises on alchemy and technical chemistry preserved in the great libraries of the Old World. Besides reproducing the original text of these precious manuscripts, these volumes contain complete translations of many treatises, analyses of the contents of others, and critical studies of their mutual relations, their sources and authorship, as well as erudite essays on the chemical knowledge exhibited in them. The six volumes form two distinct works: three of the volumes bear the title: "Collection des anciens Alchimistes Grecs," and three of them, "La chimie au moyen âge," each volume having, moreover, specific sub-titles more exactly indicating its contents.

Not having seen any adequate review of these works in English, I propose in this article to examine their scope, contents, and manner of treatment, as well as to show some of the more important changes resulting from Berthelot's historical studies. The existence of ancient Greek and Arabian manuscripts had long been known; Reuvsen, and later Leemans, of Holland, had published summaries of certain papyri preserved in Leyden, more than forty years before, but in such a fragmentary manner as merely to excite curiosity: Ferdinand Hoefer, the French historian of chemistry, and Herman Kopp, the erudite German, had made partial use of some of the manuscripts, but it remained for Berthelot to collect and compare the diverse copies, to reproduce and translate them for the benefit of students. This he could scarcely have accomplished without the aid of the French Government, both series being "published under the auspices of the Minister of Public Instruction." Government cooperation was brought about through a report made by Berthelot to

<sup>1</sup> Read before the Washington Section of the American Chemical Society, March 12, 1896.

the "comité des travaux historiques et scientifiques," and adopted by them in 1884. This report directed attention to the existence of Greek alchemical manuscripts and to the utility of their publication, owing to the great light they throw on the history of natural science, the technology of metals and ceramics, and the history of philosophy in the first centuries of the Christian era.

The difficulties of deciphering, transcribing, and editing Greek, Arabic, Syriac and Latin manuscripts were prodigious, and Berthelot was fortunate in securing scholars of eminence to assist in the task. In dealing with the Greek papyri, he was aided by Ch. Em. Ruelle, of the Bibliothèque Sainte Geneviève, Paris, and by André Berthelot, son of the editor; the Arabic scholar, Professor Houdas, and the Syriac linguist, Rubens Duval, also contributed their learning, each in his own sphere.

The "Collection des Alchimistes Grecs," opens with an "Introduction" by Berthelot, which occupies 268 pages; this forms an important contribution to the history of chemistry, based upon a critical study of the ancient treatises; he agrees with other historians in tracing the birth of alchemical ideas to Egyptians, whence they reached Europe through Greeks.

Certain Greco-Egyptian papyri, preserved in Leyden, are of the greatest interest; several of them treat of magical formulas, incantations, love philtres, dreams, and similar gnostic notions; one of them, known as "Papyrus X," is a treasury of information on metallurgical operations, at so early a period as the third century of the Christian era. It was found in a tomb at Thebes, secured by the Swedish Consul at Alexandria, Anastasi, and presented by him to the Netherlands in 1828. Berthelot conjectures it is one of the ancient Egyptian books on the preparation of gold and silver, which escaped the destruction ordered by Diocletian in 290; an order issued lest the people using them should grow rich by their art and revolt against the Romans.

This precious document contains one hundred and one chemical and alchemical recipes, followed by ten paragraphs taken from Dioscorides. The recipes are for making alloys to be used in the manufacture of cups, vases, images, and other objects of the goldsmith's art, also processes for soldering metals and superficially coloring them, besides formulas for making gold and silver inks. The text is full of grammatical errors and ignorant spellings, which show the writing to have been the work of an uneducated artisan; the recipes are not arranged in order, several appear in duplicate; they exhibit no indication of chicanery, although some of the methods are unprofitable. The

whole papyrus, in short, is evidently the memorandum-book of a goldsmith (or, silversmith), engaged in attempts to imitate gold and silver for fraudulent purposes. Only one author is cited, "Phimenas," who is probably Pammenes, author of recipes occurring also in other manuscripts. The preparation of *asem*, an amalgam of copper and tin, plays a prominent part among the recipes for imitating gold. But time forbids a full analysis of this remarkable manuscript; as a result of Berthelot's careful study of this and analogous treatises, he comes to the conclusion that the doctrines of alchemy concerning the transmutation of metals did not originate in the philosophical views of the constitution of matter, as generally supposed, but in the practical experiments of goldsmiths occupied in making fraudulent substitutes for the precious metals. The "Introduction" contains a chapter on the relations between the metals and the planets, of Chaldean origin, and constant occurrence in the early writings, which is illustrated by facsimiles of several manuscript pages. Another chapter is devoted to the figures of apparatus occurring in the treatises of the eleventh to fourteenth centuries; these include water-baths, digestors, aludels, alembics and a great variety of apparatus for distillation.

The sixth chapter of the introduction is divided into twelve sections; these deal with several Greek manuscripts, notably those preserved in the libraries of St. Mark, Venice, the Escorial, the Vatican, Rome, Gotha, and in Munich, appertaining to the eleventh to fourteenth centuries; of these we note only a few features. At the beginning of the MS. of St. Mark is one of the earliest of chemical bibliographies; it gives the title of fifty-two treatises, verily not in modern style, yet quite suggestive; among them are the following: "Emperor Heraclius, eleven chapters on the manufacture of gold." "Justinian, five chapters on the secret art." "Heliodorus, on the divine art." "Theophrastus, verses on this art." "Moses, on the diplosis (doubling) of gold." "Lexicon of the gold maker, in alphabetical order."

This association of names of Emperors of Rome, Greek classical writers and the Hebrew law giver with chemical and alchemical treatises is characteristic of the period at which they were compiled and by no means denotes actual authorship; the names of prominent men were given to the treatises in order to add to the dignity and authority of the writings. This custom prevailed as late as the sixteenth century, and in certain cases to be noted hereafter, gave rise to undeserved honors. An entire group of writings have been ascribed to Democritus, giving rise in Egypt to what may be styled the school of Democritus. A certain Zosimus of Panopolis is credited with a veritable ency-



clopedia of the sacred art, a work which occupies ninety pages of Berthelot's volume.

The Collection des Alchimistes Grecs comprises no less than 160 different treatises on the science of Hermes. Many of these are fragmentary in the extreme, extending to only six lines, and even less. All are composed in an archaic, enigmatical style, combining in one undecipherable medley, chemical terms of obscure meaning, magical formulas, astrological notions, citations from mythical authors, and mystical allusions to a philosophy long since buried too deep for present resurrection. It is not surprising that commentators early felt the need of lexicons of the sacred art, and such are preserved in these volumes; unfortunately, however, the definitions are no clearer than the words defined; one word was often used for a score of different objects and processes, and a single article was known by a dozen different names. To convey to readers any idea of these extraordinary literary productions by citations, is hardly practicable in the space available, for passages lose much when removed from their original settings. The actual chemical knowledge exhibited in these ancient manuscripts is varied, and yet indefinite, owing to the numerous obscure expressions; the authors were acquainted with a large number of ores, minerals, earthy substances, and saline bodies, as well as vegetable and animal products, but their ignorance of the mineral acids and their important derivatives, limited them to products obtained by aqueous solution, distillation and the action of heat. Of scientifically classified knowledge there is no trace; the alleged opinions of mythical writers are given as authoritative, and information is imparted in the tedious form of dialogues between philosophers, who remind one of the Scotchman's definition of metaphysicians: "Poor bodies discussing things of which they know nothing, in a language neither of them can understand." Many of the writings contain reverent acknowledgements of the Deity and other evidences of piety. There is a good deal of duplication, arising from the introduction into an essay of passages from another, generally without acknowledgement.

Berthelot remarks incidentally that the term *Philosophers' Stone* does not occur in writings earlier than the seventh century, although the central idea is much more ancient.

Each of the three quarto volumes which constitute Berthelot's "*La chimie au moyen âge*" bears an independent title; that of the first volume reads: "Essay on the transmission of the knowledge of Antiquity to the Middle Ages; transmission of technology; translations of Arabico-Latin treatises, with a new

version of the *Liber Ignium* of Marcus Graecus, and an original edition of the *Liber Sacerdotum*."

This volume covers the period from the fall of the Roman Empire to the thirteenth century, thus filling the gap between the ancient Greek alchemists and the Latin writers of the later epoch, a period which had been previously unworked or misunderstood. Berthelot finds that the transmission from the earlier to the later era was accomplished by two agencies; first through the Arabians, who succeeded to the literary and scientific wealth of the Greeks. The Arabic treatises, preserved in the Mohammedan libraries of Spain, were translated into Latin and thus became for Western nations the sources of their knowledge in medicine, alchemy, mathematics and philosophy. Some of these translations were collected and printed in the seventeenth century in the works entitled *Theatrum chemicum*, (5 vols., 1613-22), and *Bibliotheca chemica*, of Mangetus, (2 vols., folio, 1702), and Berthelot discovered in these Arabico-Latin treatises entire passages from the ancient Greek Alchemists.

The connection between the Greeks and Arabians was not however immediate, but through the Syrians, who were among the first to translate the philosophy and science of the Greeks into an oriental tongue. These Syraic versions form the subject of the second volume.

A second link between the Greeks and the Latin alchemy was more directly forged, though difficult of recognition; the processes used in industrial arts and metallurgical operations by the Greeks had been adopted by the Latins as early as the time of the Roman Empire, and this chemical technology was preserved through centuries of intellectual degradation to the beginning of the Middle Ages.

The most ancient Latin treatises on chemical technology are the *Compositiones ad tingenda*, dating from the close of the eighth century, and the *Mappæ clavicula*, written before the tenth century. These are collections of recipes for industrial processes analogous to those in the Leyden papyrus, and forming links in a chain that extends from that ancient work through the treatises of the Middle Ages to the modern "Workshop Recipes" and "Manuels Rorets." The full title of the *Compositiones ad tingenda* is as follows: [Translation.] "Recipes for coloring mosaics, skins and other objects, for gilding iron, for using minerals, for writing in letters of gold, for soldering metals, and other technical documents." The following are some of the subjects treated: The coloring of artificial stones, used in the manufacture of mosaics; the manufacture of stained glass; the dyeing of skins in purple, green, yellow and reds; the dyeing of

wood, bone and horn ; a list of ores, metals, earths and metallic oxides used in jewelry and in painting ; a number of recipes for gilding on glass, wood, skins, garments, and the metals. All these topics are treated in barbarous Latin, bordering on a species of jargon ; some were originally written in Greek and copied by ignorant scribes in Latin letters, which shows the influence of Constantinople. In one of the sections on ores, the word "vitriol" occurs for the first time, being the eighth century, and in the correct significance of an impure ferrous sulphate. A very rational grouping of substances occurs in this work, the minerals and earths are by themselves, then follow gums, rosins and other products of plants, and thirdly substances derived from the ocean, such as salt, coral and mollusks yielding purple dye. A certain recipe for writing in letters of gold is practically identical with one in the Papyrus of Leyden.

A formula for making bronze shows the origin of this name, *De compositio brandisii*, Brindes being a synonym of Brundisium, (Brindisi), a town noted in Pliny's day for its metallic mirrors.

A large part of *Compositiones ad tingenda* is reproduced in the work entitled *Mappa clavicula*, of which the earliest known manuscript dates from the tenth century. This latter treatise contains recipes for making gold, for multiplying gold and imitating the precious metal, closely resembling those of the ancient Greek papyri. In this connection cautions are given to conceal the secrets, and an incantation is prescribed to be used during the operation. Exceeding interest attaches to the fact that the use of the hydrostatic balance in analysis of an alloy is clearly described, for this proves that the knowledge of this instrument did not pass through Arabian channels, and possibly came down direct from Archimedes.

The *Liber ignium ad comburendos hostes*, by Marcus Graecus, is one of the most ancient Latin treatises on Greek fire, dating from the twelfth or thirteenth century, and is probably a translation from an earlier Greek work transmitted through Arabian channels. It deals with instructions for making Greek fire, so called, phosphorescent materials, fire-proofing substances, and the preparation of fuses and petards, composed in part of saltpeter. Greek fire itself, however, dates from the second century, B. C., and phosphorescent stones are named in the much earlier Greek alchemical manuscripts.

Berthelot devotes an interesting chapter to the discovery of alcohol. This product of distillation first appears under the name *aqua ardens*, and the term alcohol in its present signification does not occur before the middle of the fourteenth century; the

term *spiritus vini* is also comparatively modern, and *aqua vitae* seems to have been applied to alcohol for the first time by Arnald de Villanova, who died in 1314. The fact that wine yielded an inflammable substance, was, however, already noted by Aristotle, but this body was not isolated. Rhases has been given credit for acquaintance with alcohol, but this is erroneous.

The preparation of alcohol by distilling wine is, however, mentioned in a copy of the *Mappa clavicula*, written in the twelfth century, and in the *Liber ignium* of Marcus Graecus.

In attempting to trace to their origin, Latin treatises which claim to be translated from Arabic, Berthelot made the important discovery that they are fraudulent, the Arabic manuscripts having no existence. Thus the chemical works attributed to the Arabian physician Jābir ibn Hayyan (Abu Musā), commonly called Geber, are shown to be fictitious, and the great reverence paid to him as a pioneer in chemistry has been misplaced. The whole history of chemistry has been falsified by giving credit to the Arabians for knowledge which really belonged to a period five hundred years later.

Yet the historical personage Geber, who lived in the ninth century, left many treatises in Arabic, now preserved in Paris and Leyden, and the translation of these occupy 100 pages of the third volume; they are very different from the works so widely known as Geber's, which are found in Latin, French, German, and English.

In like manner the current alchemical treatises ascribed to Raymond Lully are shown to be fictitious, yet his works on philosophy in the Provençal language are extant.

The Pseudo-Arabic works in their Latin form contain, however, traces of the ancient Greek alchemical writings, and to endow them with authority the writers referred the text to mythical personages; and as these were cited by later authors who did not doubt their genuineness, the pseudo-treatises acquired undeserved renown. Students of alchemy who have been revelling in the works of Morien, Kalid, Zadith, Mary, and the collection of citations entitled *Turba philosophorum*, are loth to have their antique idols shattered, but this is the fate of every branch of human knowledge when subjected to the modern methods of searching analysis.

The second volume of "La chimie au moyen âge" has the subtitle: Syriac Alchemy, comprising an introduction, and several treatises of Syriac and Arabic alchemy from the manuscripts in the British Museum and Cambridge; text and translation."

The existence of Syriac alchemical manuscripts in the British

Museum was pointed out to Berthelot by Prof. Richard Gottheil, of Columbia University, New York City. The most important of these, entitled "The Doctrine of Democritus," was translated from Greek between the seventh and ninth centuries. It begins with a charge of self-purification, followed by a key to the symbols used in the manuscript; these signs resemble in part those occurring in the writings of the earlier Greek alchemists. The first section of the "Doctrine" is called "The Preparation of Gold," the second is called "On the Philosophers' Stone," and the succeeding parts contain a collection of recipes, processes with metals, as well as with sulfur, antimony, arsenic, and ores, analogous to the Leyden papyrus and the *Mappa davicula*. Rude drawings of apparatus accompany the text. The writer shows acquaintance with a very large number of chemical substances.

The Library of the University of Cambridge possesses a Syriac manuscript, which is a translation of portions of the Greek writings of Zosimus, Democritus, and others. It is similar in character to the preceding.

Volume III of "La chimie au moyen âge" has the sub-title: "Arabian Alchemy, comprising an historical introduction, the treatises of Crates, el-Habîb, Ostanès and Djâber from manuscripts in Paris and Leyden; text and translation."

The Arabic treatises here named are the genuine writings, not the fictitious ones known only in Latin. The first Mohammedan writer on alchemy was Khâled ben Yezid ibn Moaouïa, Prince Omeyyade, who died in 708; he is a historic personage and the reputed teacher of Djâber. Only the titles of his works have come down to us. Djâber, the Geber of the Latins, was, however, the great master of the art and enjoyed the highest reputation throughout the Middle Ages; he is credited with 500 treatises, an Oriental exaggeration. Six of these are here collected and translated. They exhibit evidence of Moslem faith on the part of the author; he shows familiarity with the hydrostatic balance, with many species of minerals (of which an ingenious classification is given), and he discourses on the changes in volume produced by heat and by cold; at the same time he admits using allegorical and obscure language in all his works. There is no reference to the mineral acids, to nitrate of silver and other chemicals that Geber is supposed to have known. Perhaps the most clever passage in his works is the following from the "Book of Mercy":—

"I saw that persons engaged in attempts to manufacture gold and silver were working ignorantly and by wrong methods; I

then perceived that they were divided into two categories, the dupers and the duped. I had pity for both of them."

Berthelot's superb volumes comprise more than 2600 pages, and much of the contents defies review. Besides these original documents he has published two works dealing in more popular style with the periods of alchemy and Middle Age chemistry. These are entitled: "*Les Origines de l'Alchimie*," (1885), and "*Introduction à l'Étude de la Chimie des Anciens et du Moyen Age*" (1889); the latter is largely reprinted in the quarto volumes; all are charmingly written, well illustrated, and well indexed.

Berthelot had extraordinary qualifications for the task and enjoyed unrivalled opportunities, and the result is a magnificent contribution to the history of chemistry, of utmost interest to the chemical student as well as to the philosopher.

H. CARRINGTON BOLTON.

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Bulletin No. 62. *Strawberries*. Kentucky Agricultural Experiment Station, Lexington, Ky. March, 1896. 16 pp.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, No. 20.]

THE EFFECT OF ACIDITY ON THE DEVELOPMENT OF THE  
NITRIFYING ORGANISMS.<sup>1</sup>

BY E. E. EWELL AND H. W. WILEY.

Received April 16, 1896.

FOR nearly two decades, both lay and scientific minds have been constantly perturbed by frequent announcements of the discovery of some new microbe that is seeking the destruction of ourselves or of our domestic animals. We have been warned to be on the alert for these deadly foes in the food that we eat, in the water that we drink, and in the air that we breathe. This general alarm has caused us to overlook many of the other important discoveries in the world of microscopic organisms. Indeed, the rapid development of our knowledge of the disease-producing organisms has been accompanied by an equally important advance in our knowledge of that multitude of microbes that are not only our friends, but are necessary to our existence. It is to one group of these more friendly organisms that we wish to ask attention. Passing over a host of species that are of importance in various agricultural industries, including those organisms that enable the farmer to draw upon the uncombined nitrogen of the atmosphere for an increase of his available nitrogenous plant food, we desire to consider the group of organisms engaged in the final stages of the process of transforming the nitrogen of dead animal and

<sup>1</sup> Read before the Washington Section of the American Chemical Society, April 9, 1896.

vegetable matter into an inorganic form suitable for the nourishment of the higher forms of plant life. It will be remembered that before the nitrogen of the fallen leaf or of a scrap of meat can be readily assimilated by the higher plants, it must undergo three stages of preparation by as many sets of organisms: first, the process of "ammonization," in which nitrogenous organic matter is decomposed, yielding as final products water, carbon dioxide and ammonia; second, the process of "nitroization," in which the nitrous ferments oxidize the ammonia to nitrous acid; third, the process of "nitration," in which the nitric ferments oxidize the nitrous to nitric acid. The organisms of the first class, the ordinary putrefactive ferments, have been known since the work of Schwann and Schultze, reported in 1839, and have been made familiar acquaintances by the more recent work of Pasteur and others. More than thirty species of bacteria and twenty species of molds and yeasts were isolated from the soil and studied in regard to their ammonizing power in 1893 by Émile Marchale, a Belgian investigator, the detailed results of whose experiments one of us (Ewell) has had the pleasure of placing before American readers in the form of a translation published in *Agricultural Science* about a year ago. Although our knowledge of this class of organisms has been greatly enlarged, their study from the standpoint of the practical agriculturist is still a very promising field of investigation.

The two remaining stages of the process, in which the ammonia formed by the putrefactive ferments is changed to nitric acid, constitute the process of nitrification, a term that is often used to include all three of the above transformations. Until very recently this was generally supposed to be a purely chemical phenomenon and quite independent of the action of living organisms. Pasteur, reasoning from analogy, had expressed the opinion that the process was dependent upon the activity of a living ferment, but it was not until the investigations of Schloesing and Müntz in 1877 that the dependence of the phenomenon upon living organisms was given experimental proof. Warrington, in England, at once repeated these experiments and obtained results that left no doubt as to the nature of the process.



The existence of a nitrifying ferment having thus been demonstrated, the contest that at once began for the honor of its isolation was such a one as has rarely been seen in the scientific world. Warington and the Franklands, in England ; Heraeus, Frank, Hueppe, Celli and Zucco, on the continent of Europe ; Jordan and Richards, in America ; all of these were prominent in this strife. As late as 1887, Frank asserted that the failure of the numerous attempts to isolate the ferment should be interpreted as evidence of its non-existence. For thirteen years the contest continued. The efforts of Warington, of the Franklands, and of Jordan and Richards, were just beginning to lead to tangible results, when, in 1890, a new worker appeared on the field in the person of Winogradsky, a Russian, working at Zurich. While many facts had been learned and many important observations had been made by the previous investigators, it was left for the worker last named to effect the first thoroughly satisfactory isolations of the nitrifying bacteria and to study them in pure cultures. These results were made possible by his finding a solid culture medium upon which these organisms grow well. Hosts of species had been isolated from the soil, from the air, and from natural waters by growth upon various solid media made by use of gelatine or agar-agar, but none of them possessed nitrifying power. Hence it had been concluded that the nitrifying ferment was unable to grow in these media, which were abandoned for the tedious dilution method. Winogradsky's medium was composed of gelatinous silica and nutrient salts. While its preparation is somewhat difficult and it apparently offers a pabulum for the development of a much greater number of microbial species than was at first supposed, nevertheless, it is the only medium available for the satisfactory isolation of the nitrous organisms. It is possible that this medium is also necessary for the isolation of some species of the nitric organism, but Burri and Stutzer<sup>1</sup> have recently studied a nitric ferment that thrives on ordinary peptone-gelatine. It is quite possible that these are the first workers that have ever given an organism growing upon peptone-gelatine an opportunity to grow in an inorganic solution containing nitrites ; *i. e.*, in such con-

<sup>1</sup> Centralblatt f. Bakteriologie u. Parasitenkunde, 1895, 1, 721-740.

ditions as would determine its ability to change nitrites into nitrates. As the demonstration of the inability of the nitrous ferment to grow upon ordinary peptone-gelatine preceded the discovery that nitrification is accomplished in two stages and by the action of two distinct ferments, it seems to have been taken for granted that the nitric organism is also incapable of growing upon the organic jelly.

We have treated the history of this subject somewhat at length, yet very briefly considering the extent of its literature. This has been done in order that what is to follow may be better understood. In the light of the researches and discoveries just outlined, the farmer must regard his fields as immense bacterial cultures. He must study their needs as well as the needs of the cultures of the higher plants whose conditions of growth he has been studying so long. In order that he may expect prompt, certain and remunerative results from the use of fertilizers containing organic nitrogen, he must make sure that his soil contains ammonizing and nitrifying organisms of the highest grade of activity, and must establish the closest possible approximation to those conditions that enable these organisms to render the greatest service in their respective roles: the conditions must be such that the process of ammonization proceeds with the smallest possible loss of nitrogen from the volatilization of the ammonia formed, or from the formation of uncombined nitrogen instead of ammonia; on the other hand, the conditions should be as unfavorable as possible for the activity of the organisms of denitrification, which reduce nitrates with the liberation of uncombined nitrogen.

Bacteria are very sensitive to the conditions under which they are grown; not only do changes in these conditions alter the rate and nature of their growth, but they also change the quantity and quality of the products formed during this growth. The principal conditions that have been found to greatly influence the growth of bacteria, are amount and quality of food, supply of moisture, the proportion of oxygen in the surrounding atmosphere, temperature, the degree of acidity or alkalinity of the medium in which they are grown, the presence of substances having a retarding or accelerating action upon their growth,

and the presence of rival or helpful species. Outside of the regions where irrigation is practiced, degrees of moisture and temperature are necessarily dependent upon meteorological conditions. In the case of the nitrifying ferments, increase of the aëration of the soil by thorough stirring has been shown to be very favorable to their highest activity. The most favorable quantity and quality of the various nutritive substances and of the other materials forming the soil, as well as the influence of the presence of other bacterial species, are still questions needing further investigation.

The proportion of alkali or acid in excess in the soil and in other media for the growth of bacteria has been shown to be a matter of the first importance. It is so constant a factor that it deserves consideration separately from the class in which it would logically fall, that of the substances having a retarding or accelerating action upon bacterial growth. The influence of the reaction of the medium upon the growth of bacteria has been very prettily demonstrated by various persons engaged in the quantitative determination of the bacteria in water. At the convention of bacteriologists, held in New York in June, 1895, George W. Fuller, of the Lawrence Experiment Station of the Massachusetts State Board of Health, presented a very interesting series of results upon this subject. We have taken the liberty to use an abridgement of one of Mr. Fuller's tables to illustrate the importance of this question.

Reaction. Cc. of normal alkali required to render one liter of the medium neutral to phenol- phthalein.	Relative number of colonies per cc of water ap- pearing upon plate cultures.		
	Sewage.	Merrimac River water.	Lawrence City filtered water.
40	6	1	2
35	16	3	3
30	45	4	8
25	64	55	46
20	100	100	100
15	106	89	92
10	101	54	60
5	98	46	43
0	86	38	35
- 5	87	26	31
-10	82	21	26
-15	55	9	15
-20	48	3	8
-25	56	1	7

The marked effect of slight changes in the reaction of the medium is rendered very apparent by this table. The most favorable reaction is one that is slightly alkaline to litmus, but still requires ten to twenty cc. of normal alkali solution per liter to make it neutral to phenolphthalein. When the acidity is either greater or less than this amount, there is a rapid falling off in the relative numbers of colonies formed.

While it was known for many years before the discovery of the nitrifying organisms, that the presence of some base is necessary to the activity of nitrification, there is very little known in regard to the exact degree of variation that can take place in the reaction of the materials undergoing nitrification without causing an interruption of the process. In the cultivation of the nitrifying bacteria in artificial media, it has been customary to add some carbonate that will neutralize the nitric acid as fast as it is formed. For this purpose, the carbonates of calcium and magnesium have been much more used because they are without influence upon the reaction of the medium until acid has been formed to decompose them. Warington<sup>1</sup> has made some experiments to determine the proportions of sodium carbonate and bicarbonate that can be used for this purpose. He reports that sodium bicarbonate can be used in the proportion of one to four grams per liter, that six grams per liter retards the activity of the ferments, and that eight grams per liter stops it entirely. The use of sodium carbonate was not attended with as good results, since one gram per liter was found sufficient to greatly retard the vigor of nitrification. This is practically all that is recorded in regard to the effect of acidity and alkalinity upon these organisms, except some statements in regard to nitrification in peaty and other soils sufficiently rich in humus to be acid in reaction. It has been reported that some soils of this type contain no nitrates whatever while in place.<sup>2</sup>

There are several ways of testing the effect of acidity upon the nitrifying bacteria. The soil itself may serve as a medium without sterilization, or it may be used after sterilization, the seedings being made from pure cultures of the nitrifying organ-

<sup>1</sup> *J. Chem. Soc.*, 1891, 59, 529.

<sup>2</sup> Chuard, *Compt. rend.*, 114, 181-184.

isms or from mixed cultures of the soil bacteria; artificial media may be seeded from pure cultures of the nitrifying organisms, from mixed cultures of the soil organisms, or with a small portion of the soil to be studied. Each of these methods has its advantages and uses. In any case, the supply of ammonia must be maintained until the process of nitrification is arrested by the acidity of the medium. When the soil is used as a medium or as the inoculating material, the experiment becomes a test of both soil and organisms, as the acid formed can have no retarding action until all of the readily salifiable base of the soil has been satisfied. When the mixed organisms of the soil are used in media containing organic matter, acid may be produced by other organisms besides the nitrifying bacteria.

As we had some forty samples of soil at our disposal during the last year for other purposes, it seemed wise to improve the opportunity to test the influence of acidity on the nitrifying organisms contained in soils from various parts of the country. The medium selected for this purpose had the following composition :

Ammonium sulphate.....	0.943 gram.
Dipotassium hydrogen phosphate .....	1.0 "
Magnesium sulphate.....	0.5 "
Calcium chloride.....	trace
Water .....	1000.0 cc.

One hundred cc. of this solution were used for each test. Before the addition of the ammonium salt, one liter of this medium requires two and six-tenths cc. of normal solution of sodium hydroxide to make it neutral to phenolphthalein. The titration was made without the ammonium salt, as the indicator is not applicable in its presence. As for every equivalent of nitric acid formed during the nitrification of this solution, an equivalent of free sulphuric acid is liberated; the nitrification of fourteen parts per million of nitrogen causes an acidity of the medium equal to two cc. of normal alkali per liter.

A summary of the results of forty-four tests is given in the following table. Twenty-two virgin soils and twenty-two cultivated soils are represented, coming from twenty-two states and territories. The tests were continued for two months and the



Florida, the results were twenty and twenty-two parts of nitrogen nitrified per million, which are very close approximations to the mean result of all the tests. The soils giving the excessive results of 130 and 170 parts per million were from Alabama, and examination has shown that they are both very rich in calcium carbonate. This, of course, explains the high results obtained.

We have "stock cultures" of the nitrifying organisms of all of these soils and hope to be able to report a repetition of these experiments with pure cultures, thus eliminating possible sources of error that may have resulted from the presence of the basic substances of the soils used as inoculating material in the series just reported. It is also desirable to determine the relative effects of various organic and inorganic acids upon the nitrifying organisms. This can only be satisfactorily accomplished by use of pure cultures. In regard to the effect of acidity upon the nitric ferments, but very little is known, except that, as we have observed above, they are not more sensitive to acidity than the nitrous ferments. The practice seems to have been to add an insoluble carbonate to the liquid media used for the growth of nitric organisms also, but we have found that this is unnecessary. The nitric organisms from all of the soils with which we have experimented, thrive well in a medium having the composition of the one given above in which sodium nitrite takes the place of the ammonium salt. There is, of course, no increase in the acidity of the medium during the growth of this ferment, as it merely changes nitrites to nitrates.

The organisms coming from various parts of the country seem to be very uniform in regard to their ability to endure acidity. If these results are again obtained when the tests are repeated with the pure organisms isolated from the different soils, the interpretation to be given to them is a very important one: these results are to be looked upon as evidence that we are to seek practical results in the study of the nitrifying organisms, not from a search for a peculiarly active species, but from a search for those conditions that are most favorable to the activity of these organisms in any given set of soil and climatic conditions.

These conclusions gain strength from the results of the recent

experiments of Burri and Stutzer,<sup>1</sup> in which they found that the mixed organisms from several samples of soil from widely separated sources assumed an almost constant nitrifying power after a series of cultivations in an artificial medium. Whether their results are to be interpreted as an evidence of constant nitrifying power in organisms from widely different soils when these organisms are cultivated in the same medium, or whether they are to be regarded only as another example of the extreme variability that bacterial species have so often been observed to exhibit, is only to be determined by extended experiments. Of high value for the confirmation of these, or of any other results obtained by means of artificial culture medium, is the re-inoculation of several soils with each of the organisms studied, noting the results during long periods of time. Both sterilized and unsterilized soils should be used for this purpose, as well as soils in which the chemical and biological conditions have been variously modified by artificial means.

We feel that the contribution that we have just made to the knowledge of this subject is almost lost in the vast unknown of the field that still remains to be explored, but this is offered as a note of the work that has been undertaken by us of attempting to make a comparative study of the microorganisms important to agriculture in typical soils from all parts of the United States. This note is not presented with any desire to preempt this field of study, for it is broad enough to monopolize the time and skill of many workers for many years to come.

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## STANDARD PRISMS IN WATER ANALYSIS AND THE VALUATION OF COLOR IN POTABLE WATERS.

BY ALBERT R. LEEDS.

Received April 16, 1896.

IN one of the first papers read before this Society and contained in its Proceedings, Vol. II, p. 1, for 1878, I have given an account of an instrument and a method for reading the quantities of ammonia obtained in nesslerizing, the instrument being termed a color comparator. It was designed primarily for this purpose only, and had its origin in the irregularities observable

<sup>1</sup> *Centralblatt f. bakteriologie u. Parasitenkunde*, 1896, 2, 105-116.



in the readings of the very minute amounts of ammonia obtained in the course of water analysis. It was subsequently found to be of great service in giving more precision to the measurement of color in potable waters, and it was used for this purpose and also for the estimation of the percentage of carbon in pig-irons, etc. The color struck by 0.01 milligram of ammonia was taken as the unit for natural waters.

The apparatus has been figured in the catalogues of the dealers for the past twenty years, and I need not describe it again here. It avoided the sources of error due to reading the tubes under different conditions and from the side, from the top and in different manners.

The light was reflected from a mirror, placed at an angle of  $45^\circ$ , down and through the middle of the tubes standing on the rack, and then by a second mirror placed below, but at right angles to the first, outward to the eye of the observer. The object was to compare the colors obtained in nesslerizing not with any one series of trial tubes prepared at the time and which might vary within wide limits, but with a coloring material contained in a wedge in connection with which the results of many readings could be plotted and so preserve a permanent standard of comparison. This wedge was placed below the aperture, next to the tube under comparison, but in order that the optical image might be similar in all respects, a tube filled with distilled water was placed above the wedge and the dark rings made by the light transmitted downward through the walls of this tube, made a part of the image also.

All that the eye then had to do was to determine whether the depth of color in two rectangular spaces, as seen in the lower mirror, each space being twenty-five mm. by ten mm. and separated by an interval of ten mm., was or was not equal. When the rack is full, which is the case in two duplicate nesslerizings, the whole of the results are before the eye of the observer at one and the same time, and twelve blocks of color strung along one after another in a horizontal line, are seen brilliantly lit up on a perfectly black ground.

But the difficulty was to obtain a suitably colored fluid to fill the prism. Naturally enough recourse was had in the first place

to the chromogenic metallic salts as being easiest to prepare of a definite strength, and as probably of the most permanent composition. To this end very many trials were made with mixtures of iron, chromium, nickel, cobalt, ferrocyanogen, gold and platinum, but all without success. When a solution gave a series of tints which were satisfactory for the lower end of the scale, it was unsatisfactory for the upper, and vice versa. Then mixtures of these salts with admixtures of coloring matters and with infusions of tea, coffee, etc., were tried and finally a solution of caramel corrected by anilin red showed as close a parallelism with the colors struck by the nesslerized ammonia as any combination experimented upon.

It was fully recognized at the time that none of these expedients fulfilled the conditions of complete parallelism of tint, permanence and ease of handling, that were desirable, and the attempt was made to substitute for the hollow wedge one of colored glass. Mr. Emil Greiner obtained many specimens of greenish-yellow, yellow and orange-yellow glass, and lent his skill in grinding them down into suitable long thin prisms. But they all failed at one or the other end of the scale, and when they were examined by the spectroscope and the difficulty was found to be due to a selective absorption of the color in the different parts of the prism, the attempt to make a satisfactory prism out of one kind of glass only was abandoned. Then thin sheets of differently colored glasses were taken, with the hope that by combination and superposition the changes of tint throughout the scale could be imitated. But at this time a very limited number of shades of color in glass could be obtained. At the present day, with the enormous development of the art of making and using glass for decorative purposes, the case is different. I am experimenting upon composite wedges, made up of wedges of different colors, and the results are promising. Certainly the obstacles to be overcome are not nearly so great as those which have been surmounted in getting rid by means of over-correction and under-correction of both spherical and chromatic aberrations in a lens. Similar composite glass wedges could be employed to estimate minute amounts of iron when a color reaction with a thiocyanate or ferrocyanide is utilized, or for

small quantities of copper or other color-giving substance.

We are only too familiar with the sources of error in the Nessler process, and every chemist at the outset of his work in water analysis is compelled to devote much time to their study. A very slight variation in the mode of preparation makes a great difference in the sensitiveness of the Nessler reagent itself. Potassium, mercury, chlorine and iodine form a large number of salts, and that their molecules are complex and constantly changing is shown by the gradual change of color of the reagent from its first pale greenish-yellow color to a light straw tint with a corresponding gain in sensitiveness. But even with a reagent which is duly sensitive in the lowest part of the scale, and with due care in seeing that the liquids are brought to a proper temperature, and with every minute precaution as to measurements, thorough admixture, etc., there still remains many uncontrollable irregularities. It frequently is the case that the color struck by 0.001 milligram of ammonia is even greater than that given by 0.002 milligram; that given by 0.002 about the same as that given by 0.003, and so on. On standing, the precipitates which settle out, are not uniform in composition, red tetragonal crystals, resembling mercuric iodide, being oft-times accompanied by dark green crystals resembling the mercurous salt. By making up a sufficiently large number of trial sets at one time, it is possible to pick out from them a series in which the differences of tint corresponding to five-tenth cc. of ammonia are, so far as the eye can judge, equal.

The same result is obtained by plotting the results of many readings on a permanent scale. As ascertained by comparison with such a scale, the sum totals of the readings are more accurate than those obtained by comparison with any one trial set made up of fluctuating and perishable members. When we consider that there is an increase both in the delicacy of the reaction and in the ability to read the color tint up to a maximum, after which both fall away again, it is probable that the most accurate method of reading would be to have a permanent scale, divided into equal parts, and to use the scale only for so much ammonia as corresponds to the differences of color which the eye is capable of estimating with certainty.

## VALUATION OF COLOR.

As has been remarked above, it was not till after the color comparator had been proposed as a means of estimating the percentage of nesslerized ammonia, that the same scale was extended to the measurement of color in waters. The article in the Journal was reprinted with illustrations in the *Zeitschrift für analytische Chemie*, 17, 276, and in the *Chemical News*, in the issue of June 7, 1878. In the issue of the latter journal for April 14, 1881, in their report upon the London water supply, Crookes, Odling and Tidy gave the following account of a similar method :

"For some time past we have been experimenting on methods of determining the colors of water, and we have this month adopted a process which, whilst it does not pretend to absolute accuracy, is a great improvement over the arbitrary 'degrees of tint depth' by which the color of water has hitherto been estimated. The process briefly is as follows :

"Two hollow wedges are filled, one with a brown and the other with a blue solution,<sup>1</sup> and these are made to slide across each other in front of a circular aperture in a sheet of metal. In this way any desired combination of brown and blue can be produced. Each prism is graduated along its length from one to forty, the figures representing millimeters in thickness of the solution at that particular part of the prism.

"On a level just below the prisms is a two-foot tube containing the water under examination, and having in front of it a circular aperture of the same size as the one in front of the prisms.

"The stand supporting the prisms and tube is placed horizontally in front of a uniformly lighted window. The observer, standing a little distance off, sees two luminous disks, the lower one illuminated by light, which has passed through two feet of water, and the upper one illuminated by light which has passed through the respective thicknesses of the brown and blue solutions.

<sup>1</sup> The solutions are made in the following way: *Brown Solution.* Dissolve ferric chloride and cobalt chloride in distilled water in such proportion that one liter of the solution contains 0.7 gram of metallic iron, and 0.3 gram of metallic cobalt. A very slight excess of hydrochloric acid must also be present. *Blue Solution.* Dissolve ten grams of pure crystallized copper sulphate in one liter of distilled water.

"By sliding the prisms sideways, one way or the other, it is easy to imitate with considerable accuracy the depth and tint of the color of the lower disk. A metal pointer affixed over the center of the upper disk shows on the prism scales the number of millimeters in thickness through which the light has passed to produce a color which corresponds to that of the water, and the results are recorded in the following way: Brown: Blue. Thus: "February 21, (New River), 20:21 means that on that date the color of New River water seen through a two-foot tube was represented by twenty millimeters of brown and twenty-one millimeters of blue solution."

Subsequently the board of London examiners abandoned the use of iron and substituted for it one of potassium dichromate.

Recently Allen Hazen, in the March number of this Journal, has advocated the use of a solution of platinic chloride, this constituent being of fixed strength, together with a solution of cobalt chloride to be added in accordance with the color sense of the observer. Possibly other chemists are employing still different solutions, and it is probably somewhat premature to expect at the present moment a concensus of opinions as to the best substances to be employed. In laying out the methods to be pursued in the examination of the waters submitted to the State Board of Health of Massachusetts (see their Report for 1890), T. M. Drown adopted the Nessler ammonia scale as the scale for color also. And in the January number of this Journal, E. H. Richards has given at length the reasons for adhering to this scale and her method of applying it through an intermediate set of colored natural waters, verified by fiduciary comparisons of certain points on the Nessler ammonia series.

In order that this renewed discussion may have the greater practical value, I shall venture to make the following suggestions:

1. That the unit of depth in the measurement of the color of water should be taken at 200 mm. This depth was used in the comparison tubes, which contain 100 cc. at the 200 mm. mark, for the reason that the same depth has already been adopted in the polariscope. Moreover, 200 mm. or eight inches, is a depth of water familiar in household use, while two feet is not, and

it is a unit that can be more conveniently applied to the unfiltered surface waters now in general use in this country, than the two-foot depth made necessary in gauging the filtered waters supplied to London and other European cities. With the general introduction of filtered waters in this country, three times 200, or 600, (which is very nearly two feet), could be used in measuring color in water that fell below  $0.2^\circ$  on the scale. The unit tube could be applied to waters showing between  $0.2^\circ$  and  $2^\circ$ . In order to preserve identity of conditions, which is of such fundamental importance in optical measurements, instead of diminishing the depth of the more highly colored waters, those between  $2^\circ$  and  $4^\circ$  could be diluted with an equal bulk of water and read in the unit depth of tube.

2. I would respectfully urge as a matter of priority and inasmuch as a very great number of measurements of color in this country are already so recorded, that the unit therein adopted which corresponds to the color struck by 0.01 milligram of nesslerized ammonia, should be retained. It may be said that for the reason already given this unit is one which cannot be precisely ascertained. But to compare lesser things with greater the same thing may be said of the meter; to rectify it in the manner originally intended, will probably never be attempted, and yet, at the same time, the meter is an universally accepted and well defined magnitude. Moreover, every time an ammonia determination is made, this unit must be ascertained and the readings for color are usually done at the same time as those of ammonia. Whether a scale is made with chromium or platinum or any other pure substance, there would be no difficulty in determining the weight of metal to be used to give the same color as that struck by 0.01 milligram of ammonia, within any such limit of precision as the eye is capable of measuring. Such a scale divided from 0 to 1 into ten equal parts and then the same divisions continued higher, could be used in the estimation of ammonia also.

3. Instead of using this scale directly, there would be great gain in using its equivalent in glass. If he desired, each chemist could test the glass scale by comparison with a fluid one made

by himself, but in daily use indestructable and properly compensated glass wedges have many advantages.

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**A METHOD FOR SEPARATING THE "INSOLUBLE" PHOSPHORIC ACID IN MIXED FERTILIZERS DERIVED FROM BONE AND OTHER ORGANIC MATTER FROM THAT DERIVED FROM ROCK PHOSPHATE.**

BY A. P. BRYANT.

Received April 13, 1896.

**D**URING the year 1895 the wholesale price of rough bone was about \$19.50 per ton in the New York markets. Ground bone brought \$22.75 per ton, and ground Charleston rock averaged \$8.12½ per ton. After allowing for the value of the ammonia, the phosphoric acid purchased in bone still costs considerable more than the same amount purchased in mineral phosphates.

Estimating 3.75 per cent. of nitrogen in the ground bone, wholesale cost 12.3 cents per pound, there would be \$9.23 worth of nitrogen per ton. This value would make the phosphoric acid in a ton of ground bone cost at wholesale \$13.52, when the same amount approximately of phosphoric acid in ground rock costs about \$8.12½ per ton.

This cheapness of mineral phosphates has led to their very general use by fertilizer manufacturers instead of bone as a source of phosphoric acid.

While the so-called Available Phosphoric Acid<sup>1</sup> of the two may be of equal value, it seems wrong to classify the phosphoric acid of mixed fertilizers insoluble in the ammonium citrate solution at the same price in the two. The Connecticut State Station's Report "Trade Value," of the organic phosphoric acid is (average) five cents per pound, while in the raw ground rock it is but two cents per pound.

It has been urged that there is no means of telling whether the "insoluble" phosphoric acid in mixed fertilizers was derived from minerals, or from bone and tankage. It was for

<sup>1</sup> That portion soluble in a neutral solution of ammonium citrate, sp. gr. 1.09, digested at 65° C. for thirty minutes.

this reason that the experiments herewith described were undertaken.

The method employed depends upon the difference in specific gravity between bone and other organic matter and the mineral phosphates. The following are the specific gravities of some of the more important compounds found in bone and in rock phosphates :

	Sp. Gr.
Bone and other organic matter, less than.....	2.0
Gypsum.....	2.3
Aluminum phosphates.....	above 2.3
Iron phosphates.....	about 2.6
Silica.....	2.65
Calcium phosphates.....	2.9 to 35.5
Fluorite.....	3.2

For the separation of the bone and organic matter from the mineral matter, a solution of mercuric iodide in potassium iodide was employed. This solution was first proposed by E. Sonstadt<sup>1</sup> in 1873, and elaborated by Thoulet<sup>2</sup> in 1878. The solution, as prepared by the writer, is as follows: Seventy-five grams of potassium iodide are dissolved in 350 cc. of warm water, and 100 grams of mercuric iodide added. The solution is filtered and evaporated in a porcelain dish over a water-bath, until a crystal of pure gypsum, sp. gr. 2.3, comes to the surface. The solution is then diluted at 15.5° C. until the gypsum is of the same density as the solution, scarcely floating or sinking. The solution is now at specific gravity 2.3, and should be diluted to specific gravity 2.26 according to the formula  $V' = \frac{V(D-D')}{D'-1}$

where  $V'$  is the volume of water to be added,  $V$  the volume of the solution,  $D$  its specific gravity 2.3, and  $D'$  the desired specific gravity 2.26. The specific gravity should be verified by use of the picnometer.

The separating solution should be placed in a small flask of about 100 cc. capacity, fitted up on the same plan as a wash bottle. The amounts given above will make about 100 cc. of solution.

<sup>1</sup> *Chem. News*, 29, 127.

<sup>2</sup> *Compt. Rend.*, Feb. 18, 1878.



The tube for making the separation may be as elaborate as desired. A very good form is described by S. L. Penfield in the *American Journal of Science* for Dec. 1895. The following has given excellent satisfaction in these experiments. A glass tube, a broken burette for example, about one and three-tenths cm. internal diameter and twenty cm. long is connected by means of a short piece of rubber tubing, with a tube of similar diameter, closed at one end and about seven cm. in length. See Fig. 1.

The material to be separated is placed in the tube and fifteen or twenty cc. of the separating solution added, after which the tube is stoppered and shaken thoroughly. The sides of the tube are now washed down with more of the solution; after standing for five minutes, the bottom part or bucket should be tapped smartly to release any light portions carried down with the heavy material, and a jet of the solution blown against the matter floating at the top, to dislodge any heavy particles. The tube is then let stand till the solution is clear, all matter having gone to the top or bottom. This will usually take from forty minutes to an hour in finely ground mixed fertilizers or rock superphosphates.

The rubber tube is now tightly clamped with a screw pinch-cock, separating the heavy material from the light. A beaker is placed beneath the tube, and the lower tube or bucket is removed, the fingers being encased in rubber finger-tips, as the separating solution cracks the skin. The tube and contents are brought on a dry filter and the liquid filtered back into the supply flask. Water is then used, the first washings being saved and evaporated down to a specific gravity of 2.26 again. The light portion is treated in a similar manner, care being taken to get all particles out of the tube at the last.

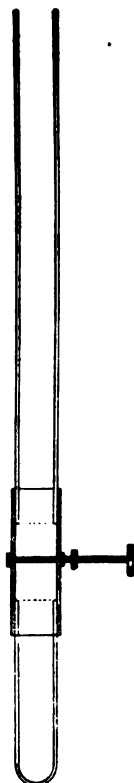


Fig. 1.

At first it was not supposed necessary to have any fixed specific gravity, but as will be seen by the following table, it is

important that the specific gravity should be somewhere about 2.26. The exact reason for this is not in the province of this paper to decide, but seems to be owing to the low specific gravity of the aluminum phosphates.

The plan of the experiments carried on was to take a fertilizer known to contain nothing but organic matter as a source of phosphoric acid, and a mixture of South Carolina and Florida phosphates, both the raw rock, and the acidulated product. These were analyzed and then mixed in different proportions and treated with the separating solution.

In the first experiment two grams of the mixture were treated with 100 cc. of the the neutral ammonium citrate solution (sp. gr. 1.09), and digested for thirty minutes at 65° C., shaking every five minutes. After filtering, the dried insoluble residue was separated as carefully as possible from the filter paper and treated as previously described. As will be seen by reference to the table following, this method, though most desirable, was given up owing to the large proportion of phosphoric acid left on the filter paper.

The next attempt was to treat the mixed fertilizer directly with the separating solution, and was also abandoned owing to soluble matter in the fertilizers which destroyed the separating solution.

These two experiments showed two things clearly, that the fertilizer cannot be treated with ammonium citrate solution before separating, and that the matter soluble in water must be removed before separating.

To obtain this latter end and expose the minimum amount of filter paper, the inner tube of a fat extraction apparatus was used, such as was described by Prof. S. W. Johnston.<sup>1</sup> These tubes are used by the Storrs (Conn.) Agricultural Experiment Station, and are made for them by Whitall, Tatum & Co., New York. The tube is about fifteen cm. in length and two and five-tenths cm. internal diameter, slightly contracted at one end, which has a rim so that a piece of filter paper reinforced on the outside with cheese cloth, can be tied on. (Fig. 2.) The method is as follows :

<sup>1</sup> *Am. J. Sci.*, 13, 190, 1877

Two grams of the raw or mixed fertilizer are transferred to the "extraction" tube and extracted with nearly 250 cc. of hot water, as for water soluble phosphoric acid determination. The tube and contents are placed in a drying oven, and when thoroughly dry the filter paper is taken off and all matter carefully removed with a spatula and brush. Any fine sediment adhering to the glass may be removed by a rubber tipped glass rod.



The material is now transferred to the separating tube Fig. 2. and treated as before described.

The light portion and heavy portion are treated separately with ammonium citrate solution, and the insoluble phosphoric acid determined in the usual way. That in the "light" comes from bone, tankage or other organic matter, that in the "heavy" from minerals.

The following is a tabular statement of the results of the experiments :

Material.	Total $P_2O_5$ .	Insoluble $P_2O_5$ .
Prepared mixed fertilizers <sup>1</sup> .....	10.75	2.56
Mixed Florida and Carolina raw rock.....	27.51	24.36
Mixed Florida and Carolina dissolved rock.	16.23	0.77

PERCENTAGE OF PHOSPHORUS PENTOXIDE FOUND IN THE HEAVY AND LIGHT PORTIONS AND LEFT ON THE FILTER PAPER.

No. of experiment		Specific gravity.	Light.		Heavy.		Left on paper.	Total.	
			Theoretical.	Found.	Theoretical.	Found.		Theoretical.	Found.
Treated with ammonium citrate before separating.									
1	Mixture A 1 .....	2.46	1.28	1.79	12.18	8.33	2.66	13.46	12.78
2	Mixture B 2 .....	2.46	1.28	2.02	0.39	0.43	0.44	1.67	2.89
3	Mixture A 1 .....	2.46	1.28	1.83	12.18	8.33	2.66	13.46	12.82
4	Mixture A 1 .....	2.35	1.28	1.52	12.18	9.68	2.66	13.46	13.86
5	Mixture B 2 .....	2.35	1.28	1.66	0.39	0.49	0.44	1.67	2.59
Separated before treating with ammonium citrate.									
6	Mixture B 2 .....	2.22	1.28	0.93	0.39	0.70	trace	1.67	1.63
7	Mixture A 1 .....	2.26	1.28	1.38	12.18	11.65	0.12	13.46	13.15

<sup>1</sup> Containing acidulated bone, tankage, dried blood, sodium nitrate and potassium sulphate.

No. of experiment.		Specific gravity.	Light.		Heavy.			Total.	
			Theoretical.	Found.	Theoretical.	Found.	Left on paper.	Theoretical.	Found.
8	Mixture C 3 .....	2.26	1.28	1.63	6.28	6.03	0.06	7.56	7.72
9	Mixture B 2 .....	2.26	1.28	1.18	0.39	0.65	trace	1.67	1.83
10	Mixture A 1 .....	2.26	1.28	1.28	12.18	12.03	0.12	13.46	13.43
11	Mixture C 3 .....	2.26	1.28	1.35	6.28	6.08	0.06	7.56	7.49
12	Mixture B 2 .....	2.26	1.28	1.11	0.39	0.48	trace	1.67	1.59
13	Mixture A 1 .....	2.26	1.28	1.24	12.18	12.07	0.12	13.46	13.43
14	Mixture C 3 .....	2.26	1.28	1.15	6.28	6.09	0.06	7.56	7.30
15	Pre'd mixed fertiliz'r	2.26	2.56	2.51	....	....	trace	2.56	2.51
16	Dissolved rock.....	2.26	...	...	0.77	0.70	trace	0.77	0.70

1 Mixture A, 1.0 gram prepared mixed fertilizer.

" " 1.0 gram raw Florida and Carolina rock.

2 Mixture B, 1.0 gram prepared mixed fertilizer.

" " 1.0 gram dissolved Florida and Carolina rock.

3 Mixture C, 1.0 gram prepared mixed fertilizer.

" " 0.5 gram raw Florida and Carolina rock.

" " 0.5 gram dissolved Florida and Carolina rock.

Of the above analyses, the first five were tentative, the method and manipulation were experimental, and the results were unsatisfactory. They show, however, that a specific gravity of 2.46 or 2.35 is too heavy for the proper workings of this method, and that when treated with ammonium citrate solution before separation, at least twenty per cent. of the phosphoric acid is lost through the adherence to the filter paper.

The sixth analysis shows that a specific gravity of 2.22 is too light, and matter which should rise to the top sinks to the bottom. Nos. 7 to 14 show that the method as finally elaborated, is quantitative and apparently reliable and capable of being put into regular use as a method of testing the source of the insoluble phosphoric acid in mixed fertilizers. The attempt was made to treat first with ammonium citrate, and filter through the extraction tube above described, in order to expose less filter paper, but the solution would not filter at all.

No. 15 was a sample of mixed fertilizer containing acidulated bone, tankage, dried blood, sodium nitrate and potassium sul-

phate, and formed the source of the "light" phosphoric acid in the above experiments. When treated with the separating solution (after dissolving out salts soluble in water) everything rose to the top with the exception of a very small amount of some material, either calcium sulphate or silica, as there was no trace of phosphoric acid in it. The solution was perfectly clear in ten minutes.

No. 16 was the acidulated Carolina and Florida rock used in the above experiments. When treated with the separating solution, a small amount came to the top. There was, however, no trace of phosphoric acid in this portion. It took an hour for the solution to become clear, showing the presence of some substance, probably calcium sulphate and aluminum phosphates, of specific gravity but little higher than that of the solution, namely, 2.26.

The method of analysis were those of the Association of Official Agricultural Chemists.

#### SUMMARY.

The following method is proposed for separating the insoluble phosphoric acid in mixed fertilizers derived from bone, tankage or other organic matter, from that derived from mineral phosphates.

#### SOLUTIONS AND APPARATUS.

*Separating Solution* : Seventy-five grams of potassium iodide and 100 grams of mercuric iodide are dissolved in 350 cc. water and evaporated over a water-bath to a specific gravity of 2.26. This solution should be kept in a small flask arranged like a wash bottle.

Other solutions necessary to determine available and total phosphoric acid.

*Separating Tube* : Two tubes one and three-tenths cm. internal diameter, one seven cm. in length, closed at one end, the other twenty cm. long. These are connected by a piece of stout rubber tubing, so that the lower part or bucket, can be separated by a screw pinch-cock from the upper portion.

*Extraction Tube* : A tube two and five-tenths cm. internal

diameter, slightly contracted at one end, which has a rim over which filter paper and cheese cloth can be tied.

Other apparatus as for available and total phosphoric acid determinations.

*Manipulation* : Two grams of the substance to be examined are transferred to the extraction tube and washed with from 100 to 225 cc. of hot water, depending upon whether or not water soluble phosphoric acid is to be determined. Dry thoroughly, remove substance carefully, using spatula, brush, and rubber tipped glass rod, and transfer to a separating tube. Add fifteen to twenty cc. of the separating solution, shake thoroughly and wash down the sides of the tube with a jet of the solution. After standing five minutes tap the lower part or bucket smartly with the finger, to release any light portion carried down with the heavy, and stir up the matter on top with a jet of solution.

Let stand until the solution is clear, or for one hour, clamp the rubber tube, place a beaker under the bucket, which is carefully removed, the fingers being encased in rubber finger tips. Filter the solution back into the supply flask, wash thoroughly, saving the first washings for evaporation to a specific gravity of 2.26 again, and treat for insoluble phosphoric acid in the usual way. The light portion is treated in a similar manner. If desired, the heavy and light portions can be treated as for total phosphoric acid, thus determining all of the phosphoric acid derived from inorganic and organic sources respectively, except the water soluble.

MIDDLETOWN, CONN.

## SOURCES OF ERROR IN VOLHARD'S AND SIMILAR METHODS OF DETERMINING MANGANESE IN STEEL.<sup>1</sup>

By GEORGE AUCHY.

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**V**OLHARD'S method of determining manganese is generally considered a very accurate one; nevertheless, that the

<sup>1</sup> In this Journal, 18, 406, I omitted to state a precaution used, in the manner of performing Drown's sulphur method there described. The solution from the Troilus' bulb is heated to boiling (preferably with the previous addition of permanganate solution) before filtering into it the hydrochloric acid solution from the graphitic residue. This is to oxidize any sulphur that may be present as sodium sulphide.

accuracy of the process is strictly dependent upon certain conditions and precautions not pointed out by the author, and not generally recognized (so far as the writer is aware) seems proved by the experience with the method and with Stone's modification of it, which follows :

#### STONE'S MODIFICATION.

Mr. Geo. C. Stone makes a very considerable saving in time by omitting the evaporation with sulphuric acid, and precipitating the iron immediately with zinc oxid as soon as solution of the drillings in nitric acid is effected.<sup>1</sup> But in Volhard's original article, as also in Blair's Chemical Analysis of Iron, it is directed to destroy the carbonaceous matter by evaporation to dryness and strongly heating, or by evaporation with sulphuric acid till fumes of the latter come off, and as previous to the appearance of Mr. Stone's paper the writer, on testing this point by dissolving in sulphuric acid with enough nitric added to oxidize the iron and help effect the solution of the drillings and omitting the evaporation, had obtained results several hundredths higher (although Volhard's objection to organic matter is that it hinders the balling together of the manganese dioxide in titration) than those obtained from the same samples by the regular process, it was judged that this precaution was not a useless one ; and after reading Mr. Stone's article it was therefore considered well, as a precaution, to test his process also in this particular, and for that purpose the following determinations were made :

TABLE I.

No.	Carbon. Per cent.	Volhard's method. Per cent.	Stone's modification. Per cent.
476	0.585	0.46	0.53
495	0.80	0.57	0.65
503	0.228	0.423	0.45
505	0.225	0.49	0.52
483	0.17	0.43	0.51
486	0.185	0.54	0.61
507	0.315	0.44	0.44

<sup>1</sup> This Journal, 18, 228. Mr. Stone finds that hydrochloric acid solution also works well.

The results of Stone's method were very considerably higher than those by the regular method, except in the case of 507. But in the case of 507 it was noted that in making the precipitation of the iron by the zinc oxide a large excess had been accidentally used, while in all the other determinations the zinc oxide had been added in amount sufficient to precipitate the iron merely; and it was therefore thought advisable to see whether the considerable differences in the results by the two methods—Volhard's and Stone's—was not due to this fact (insufficient neutralization in the latter) before attributing it to the organic matter undestroyed in Stone's method. The above determinations were therefore repeated, using in each case not only enough zinc oxide to coagulate the solution and precipitate the iron as directed, but also enough in excess of this amount to turn the brownish red color of the iron precipitate to a light brown. The results follow:

TABLE II.

No.	Carbon. Per cent.	Volhard. Per cent.	Stone. Zinc oxide to coagulation. Per cent.	Stone. Zinc oxide in large excess. Per cent.
503	0.228	0.423	0.45	0.45
505	0.225	0.49	0.52	0.51
483	0.17	0.43	0.51	0.45
483	0.17	0.43	0.51	0.45
486	0.185	0.55	0.61	0.58
486	0.185	0.54	0.61	0.58
476	0.585	0.46	0.53	0.47
495	0.80	0.57	0.65	0.60
471	0.105	0.38	....	0.40
480	0.10	0.35	....	0.36
493	0.57	0.46	....	0.47
507	0.315	0.435	....	0.44
153	0.50	0.64	....	0.70
153	0.50	0.64	....	0.67
153	0.50	0.64	....	0.69
155	0.40	0.56	....	0.56

These results show that when the zinc oxide is added merely to coagulation and precipitation of the iron, leaving the solution probably faintly acid, the manganese is afterward precipitated, not according to the theoretical formula, but with result too high;



and that to insure the correct precipitation of the manganese it is necessary to add the zinc oxide in large excess, so that the solution is thoroughly neutralized when titrated.

It will, however, be noted that with this precaution, observed results in the table are nevertheless a few hundredths per cent. higher than by Volhard's method.<sup>1</sup> Is this difference due to the undestroyed carbonaceous matter? It was thought probable, but to make sure, some of the tests were repeated with oxidation of the carbonaceous matter by addition of lead dioxide to the boiling nitric acid solution of the drillings (the excess destroyed by ferrous sulphate and the excess of the latter oxidized by continued boiling of the nitric acid solution).<sup>2</sup> These results should be lower if carbonaceous matter has any influence. They were not lower, as the following table shows, and hence it is indicated that carbonaceous matter does not interfere. It is true that in one case (483) the result obtained by oxidation of the carbonaceous matter is lower, but the reason for this will appear later on.

TABLE III.

No.	Carbon. Per cent.	Stone.	Stone.
		With carbon not oxidized. Per cent.	With carbon oxidized. Per cent.
480	0.10	0.36	0.37
507	0.315	0.44	0.44
155	0.40	0.56	0.55
155	0.40	0.56	0.57
155	0.40	0.56	0.56
155	0.40	0.56	0.56
153	0.50	0.70	0.68
483	0.17	0.45	0.41

Since the slightly high results obtained by Stone's method, in Table II., are not due to the undestroyed carbonaceous matter, they must be due to the fact of titration in nitric acid solution. The following determinations of manganese in solutions containing no organic matter, and in which the amount of mangan-

<sup>1</sup> It was later seen that the accuracy of the regular Volhard process was also dependent upon certain conditions; and the results by this method, given in these two tables, are the corrected results obtained later by checking with the color method according to Table VI. So that in Tables I. and II. the comparison is really with the color method rather than with Volhard's method. As explained under Table VI., there was not enough left of the samples for gravimetric tests. For a comparison of Stone's method with the gravimetric see Table XI.

<sup>2</sup> The lead dioxide and the ferrous sulphate used were tested for manganese.

ese was known (made by taking definite amounts of standard permanganate solution) are confirmatory of this conclusion :

TABLE IV.

No.	Manganese taken. Per cent.	Manganese found. Per cent.	No.	Manganese taken. Per cent.	Manganese found. Per cent.
1	0.40	0.41	8	0.40	0.42
2	0.40	0.41	9	0.80	0.81
3	0.40	0.41	10	0.80	0.82
4	0.40	0.41	11	1.20	1.24
5	0.40	0.41	11	1.20	1.22
6	0.40	0.41	13	0.80	0.81
7	0.40	0.42	14	1.20	1.22

Here, then, is a second precaution to be observed in Stone's method : a correction of the result by one or two hundredths per cent. must in each case be made. But still other precautions are necessary, as will appear.

## VOLHARD'S METHOD.

The fact brought out by working upon Stone's method, that titration in faintly acid (nitric) solution gives too high results led to the suspicion that the same was also true of Volhard's regular method (sulphuric acid solution). The following tests were made :

TABLE V.

No.	Volhard. Zinc oxide added to coagulation.	Volhard. Zinc oxide in large excess.
490	0.49	0.39
490	0.49	0.39
490	0.49	0.39
490	0.49	0.49
476	0.51	0.46
507	0.49	0.44
483	0.45	0.41
503	0.45	0.41
471	0.41	0.38
289	0.42	0.40
289	0.42	0.40
493	0.51	0.44
505	0.50	0.46
155	0.58	0.49
155	0.58	0.56
289	0.42	0.41
153	0.66	0.64

Results of the first column were obtained by adding zinc oxide till the solution stiffened and the iron all precipitated. In the second column of determinations the zinc oxide was added in sufficient excess of this amount to make the color of the precipitated iron a light brown. The differences in the results were supposed to be due to this fact already noted in considering Stone's method—that titration in slightly acid solutions gives too high results. But a suspicion arose that these differences might, in part at least, be due to manganese being mechanically carried down with the iron when the large excess of zinc oxide was used. The obvious test of this would have been to make gravimetric determinations in the samples used in the last table. But, unfortunately, there remained but very little drillings of each of the samples. So the next best thing was done, and a standard manganese sample was prepared, and the determinations of these samples of the last table made by the color method: in each case making a number of tests and taking the average. Results:

TABLE VI.

No.	Volhard. Zinc oxide to coagulation.	Volhard. Zinc oxide in large excess.	Color method.
490	0.49	0.39	0.48
507	0.49	0.44	0.435
483	0.45	0.41	0.43
503	0.45	0.41	0.423
471	0.41	0.38	0.38
289	0.42	0.40	0.40
492	0.51	0.44	0.46
503	0.50	0.46	0.49
155	0.58	0.49	0.56

Showing that when the neutralization with zinc oxide is carried only to the point of precipitating the iron the result will invariably be from 0.01 per cent. to 0.05 per cent. too high; while on the other hand, if the zinc oxide be added in excess of this amount, the result *may* be too low, and very much too low from the precipitation of manganese with the iron. These points would have been more certainly and satisfactorily proved, however, had the comparison of the Volhard results been made directly with results by the gravimetric process instead of by the

color test. In the following table such comparisons with the gravimetric method—in a new lot of steels—are made, and confirm the conclusions drawn from the preceding table. In the second column of tests, the neutralization was performed in a way not to precipitate the manganese. In the third column of tests, neutralization was purposely performed in a way most favorable to the precipitation of manganese with the iron.

TABLE VII.

No.	Zinc oxide to coagulation. Per cent.	Excess of zinc oxide. The excess added after filtration of ferric oxide. Per cent.	Excess of zinc oxide. Added suddenly to the iron solution. Per cent.	Gravimetric method. Per cent.	Color method. Per cent.
451	0.56	0.51	0.51	0.52 (acetate)	0.53
452	0.46	0.44	0.44	0.43 "	0.435
453	0.46	0.46	0.37	....	0.425
454	0.47	0.47	0.44	0.46 (Ford)	0.45
493	0.51	0.46	0.44	....	0.46
456	0.45	0.41	....	0.41 (Ford)	0.43
466	0.54	0.49	....	0.485 "	0.49
481	0.48	0.45	....	0.455 "	0.46
153	0.66	0.64	....	....	0.64
000	1.30	....	....	1.25 <sup>1</sup>	....

Insufficient neutralization gives high results. Complete neutralization *suddenly*, gives low results. Here then is the explanation for the low result of Table III (483); the ferric oxide precipitate had carried down some of the manganese.

The remedy is obvious. It is to carefully avoid an excess of zinc oxide at the time of precipitating the iron; adding the necessary excess to the aliquot part of the filtrate from the ferric oxide, taken for titration—filtering off the undissolved zinc oxide before titrating. But this procedure involves considerable extra work. And it does not seem necessary, if certain precautions be taken, to filter off the ferric oxide before adding the excess of zinc oxide. For it is reasonable to suppose that it is the *sudden* addition of the zinc oxide in excess to the rather concentrated solution that carries down the manganese. If the iron be first precipitated carefully by the gradual addition of zinc oxide, avoiding an excess, we have seen that no manga-

<sup>1</sup> Made by Williams, of Boston.

nese is carried down. If now, the solution be diluted, mixed, and the ferric oxide be allowed time to begin to settle, there seems no reason why the further addition of an excess of zinc oxide should then precipitate manganese. That it does not is evidenced by the preceding table, second column of results, last four results, which were obtained in this way. Also all of the determinations by Stone's modification in Table XI.

In the determination of the results of the third column of results in the preceding table, pains were taken to add the excess of zinc oxide as suddenly as possible; nevertheless, only three out of the five results are low, showing (as also do the results of Table VI.) that manganese is not invariably carried down by such a procedure. In Stone's modification the tendency to a precipitation of manganese with the iron seems less; for of the numerous results by that method (obtained before the necessity of any precaution in precipitating the ferric oxide was known) only one is low. But in both methods the neglect of the precaution to *thoroughly* neutralize with zinc oxide almost invariably gives results more or less above the truth.

Taught suspicion by the experience thus far had, it was resolved to test every step in the method; and the following determinations were made to see if the temperature of the liquid at the time of neutralization with zinc oxide had any influence upon the result:

TABLE VIII.

Solution heated to boiling with the zinc oxide.			Zinc oxide to cold solution.		
No.	Manganese taken. Per cent.	Manganese found. Per cent.	No.	Manganese taken. Per cent.	Manganese found. Per cent.
1	0.40	0.49	1	0.40	0.40
2	0.40	0.44	2	0.40	0.40
3	0.40	0.43	3	0.40	0.40
4	0.40	0.47	4	0.40	0.40
5	0.40	0.42	5	0.40	0.40
6	0.40	0.41	6	0.40	0.39
Solution merely warm.			7	0.40	0.40
1	1.20	1.22	8	0.40	0.41
2	0.80	0.83	9	0.40	0.40
			10	0.80	0.80
			11	1.20	1.20

These results show that neutralization must be performed in the cold. The writer had always practiced this precaution, though for no well defined reason.

The second series of results in the table also show that there is no tendency to slightly high results, as is the case when titration is done in nitric acid solution (Stone's method).

Volhard, in his article, states that the precipitated manganese dioxide is mixed with protoxide unless some metallic base like zinc oxide, lime, magnesia, etc., be present; and, therefore, in the following experiments on this point it was expected that the results would be poor, since the amount of zinc oxide present was purposely kept as low as possible by making the neutralization first with sodium carbonate, and then cautiously adding sulphuric acid till slightly acid, the slight excess of acid being then neutralized with zinc oxide.

TABLE IX.

No.	Taken. Per cent.	Found. Per cent.	No.	Taken. Per cent.	Found. Per cent.
1	0.40	0.41	4	0.40	0.41
2	0.40	0.42	5	0.40	0.42
3	0.40	0.40			

These results seem to show that this is not a very important source of error. In Särnström's method the point is entirely disregarded.

Five determinations made with five cc. free sulphuric acid (two to one) at time of neutralization with zinc oxide give, instead of the theoretical 0.40 per cent. taken, respectively 0.40 per cent., 0.42 per cent., 0.41 per cent., 0.41 per cent., 0.41 per cent.

With six cc. free acid, 0.40 per cent., 0.41 per cent.

With eight cc. free acid, the results of Table VIII.

#### SÄRNSTRÖM'S METHOD.

Messrs. Mixer and DuBois recommend this method for iron ores,<sup>1</sup> and give results showing its accuracy. In this method zinc oxide is not used, the neutralization (hydrochloric acid

<sup>1</sup> This Journal, 18, 385.

solution) being effected entirely by sodium carbonate, with care not to add it in greater amount than necessary to precipitate the iron, and the subsequent titration is done without filtering off the ferric oxide thus precipitated. This manner of neutralization leaves the solution not thoroughly neutralized, and from the foregoing results of this article we should expect high results from Särnström's method. The results given by Messrs. Mixer and DuBois are, however, excellent results; and this indicates either that neutralization with sodium carbonate in hot hydrochloric acid solution is not attended with the same phenomena as neutralization with zinc oxide in nitric and sulphuric solutions, or that in the former process there is a greater tendency of the manganese to precipitate with the iron, and that the error from this source counterbalances the error from titrating in faintly acid and hot solution. But the uniform excellence of the results given by Messrs. Mixer and DuBois points to the former as the more likely supposition. The method was briefly tested by taking standard manganese solution. Instead of 0.40 per cent. manganese taken in one case, 0.44 per cent., and in another 0.38 per cent. was obtained. But the test was not a fair one as there was no iron present to give the exact point of neutralization as obtained in the regular working of this method. Ferric chloride should have been added, but none was at hand, and the writer postponed further examination of the method for the reason that (as explained by Messrs. Mixer and DuBois) it is not well adapted to the analysis of steel.

#### COLOR METHOD.

The color method has no kinship to Volhard's, and its consideration is therefore hardly relevant here. But, nevertheless, as it was found necessary in the course of this work to make determinations by this method for comparison with others obtained by Volhard's method in samples almost used up, it might perhaps be just as well to give these color results in detail, as showing the limits of error in the process when performed by one not an expert in its use.

TABLE X.

No.	First reading. Per cent.	Second reading at a higher dilution. Per cent.	Volhard or gravi- metric method. Per cent.
289	0.40 0.395 0.40	0.40 0.39 ....	0.40 Volhard.
153	0.63 0.61 0.639	0.64 .... 0.65	0.64 Volhard.
503	0.552 0.564 0.572 0.543	0.547 0.560 0.586 0.555	0.56 Stone.
503	0.43 0.426 0.42 0.42	.... 0.416 0.425 0.42	0.423 Volhard.
505	0.495 0.49 0.485 0.495	0.49 0.48 0.485 0.495	0.49 Stone.
483	0.44 0.425	0.425 0.425	0.43
486	0.53 0.54	0.534 0.546	0.54
471	0.38 0.39	0.37 ....	0.38 Stone.
490	0.48 0.48	0.48 0.486	0.48
493	0.438 0.47 0.468	0.445 0.466 0.47	0.46 Volhard.
507	0.43 0.43	.... 0.44	0.435 Stone.
466	0.488 0.497 0.49	0.472 0.498 0.475	0.49 Gravimetric.
481	0.50 0.455 0.47 0.446 0.476	0.49 0.454 0.46 0.446 0.47	0.469 Gravimetric.
453	0.43 0.416 0.449 0.427	0.426 0.425 0.446 ....	0.425 Stone.
456	0.417 0.416 0.417	0.42 0.428 0.414	0.43 Gravimetric.
451	0.545 0.53 0.54 0.52 0.537 0.535	0.56 0.53 0.54 0.52 0.525 0.545 0.531	0.52 Gravimetric.



The results in the table by Volhard's and by Stone's method were obtained by an observance of precautions given—correction of 0.02 per cent. in results by the latter method, thorough neutralization by zinc oxide, etc.

It will be seen that color method results are quite accurate if a number of color comparisons be made and the average taken. But if only one test be made the variation may occasionally be 0.02 to 0.03 per cent. But in these determinations the boiling was all done over the naked flame. Closer results can perhaps be had by using the calcium chloride bath for this purpose, as directed in Blair's Chemical Analysis of Iron.

#### RECAPITULATION.

The sources of error, then, in Volhard's process, as indicated by the foregoing experiments, are :

1. The incomplete neutralization by zinc oxide, giving usually high results.
2. The too sudden addition of the necessary excess of zinc oxide, giving frequently low results.
3. The titration in nitric acid solution giving results 0.01 or 0.02 per cent. too high.
4. Neutralization by zinc oxide in hot solution, giving high results.

With regard to the first of these sources of error it may be remarked that Volhard recommends slightly acidifying with nitric acid before titration—to oxidize organic matter. But whatever organic matter may be present capable of being oxidized by nitric acid has already been oxidized, and the organic matter and proto salts present in the sodium carbonate and zinc oxide used for neutralization is best determined by a blank or dummy test, or better by performing the process with a convenient measured amount of standard permanganate decomposed by hydrochloric acid. Besides the error from titrating in faintly acid solution, a further objection to acidifying with nitric acid is that the manganese dioxide precipitated by titration collects as a film on the glass and obscures the end reaction.

Stone's modification is much easier and quicker than the regu-

lar Volhard method; not only because the evaporation to dryness with sulphuric acid is dispensed with, but also, as Mr. Stone points out, because in nitric acid solution the precipitated ferric oxide settles so readily and completely that the filtration from it may be omitted, the clear liquid being decanted from the precipitate. In sulphuric acid solution the precipitated ferric oxide does not settle readily enough for this, and thus considerable time is taken up in making folded filters, and the filter paper used adds appreciably to the expense of the method.

Mr. Stone performs the neutralization entirely with commercial zinc oxide, and this is doubtless the reason that his results have always been satisfactory, and he has noticed no necessity for the precaution of thorough neutralization; for in neutralizing altogether with zinc oxide, in the hurry of every day work one would naturally get a large or a considerable excess of it used, even if not recognizing the necessity for such an excess. And as to the precipitation of manganese with the iron, the work in this article would seem to show that to be an exceptional occurrence with nitric acid solution, although of frequent occurrence in sulphuric acid solution if caution be not used in the neutralization. But as regards neutralization, the writer considers it more advantageous to use sodium carbonate, or common sal soda first, finishing up with zinc oxide emulsion, for sal soda is much cheaper than commercial zinc oxide. But, as before mentioned, the manganese, organic matter, and proto salts in these reagents, if any be present, must be allowed for.

Mr. Stone takes 100 cc. for titration. But 250 cc. is perhaps preferable on the score of greater accuracy. The writer finds it convenient to use permanganate of strength exactly 0.0056, taking always three and three-tenths grams of the drillings for analysis. The reading of the scale on the burette then at once gives the percentages of manganese without calculation, except a division by ten.

For the convenience of those unfamiliar with the process details briefly follow, with the precautions found to be necessary in this article printed in *italics*. Three and three-tenths grams of drillings. Dissolve in fifty cc. nitric acid, sp. gr. 1.20. Wash

into a 500 cc. measuring flask. Add about two-thirds of the amount of sal soda solution necessary to a complete neutralization. *If not cold, cool.* Add zinc oxide emulsion till solution stiffens, *avoiding an excess.* Dilute to about three-fourths of the capacity of the flask, mix and let stand till the ferric oxide begins to settle. See that the solution is colorless. *Add considerable excess of zinc oxide emulsion.* Mix. Dilute to mark. Insert stopper. Mix. Transfer to dry beaker. Mix again. Let settle, and pour off 250 cc. Titrate in 500 cc. Erlenmeyer flask, (first heating to boiling) with permanganate of strength 0.0056. Make the necessary deduction for impurities in the sal soda and zinc oxide. Divide the number of cubic centimeters permanganate taken by ten. *Deduct 0.02 per cent.*

Following are some comparisons of results by this method with results by Volhard's method, gravimetric method, and color method:

TABLE XI.

No.	Volhard with all precautions. Per cent.	Stone with all precautions. Per cent.	Gravimetric. Per cent.	Color. Per cent.
1451	0.51	0.51	0.52	0.53
452	0.44	0.42	0.43	0.435
453	0.46	{ 0.42 0.43	....	0.425
453	0.47	0.45	0.46	0.45
493	0.46	0.47	....	0.46
466	0.41	0.41	0.41	0.43
466	0.49	0.49	0.485	0.49
481	0.45	0.46	0.455	0.469
153	0.64	0.65	....	0.64

A SIMPLE FORM OF GAS REGULATOR.<sup>1</sup>

BY LUDWIG SAARBACH.

Received April 17, 1896.

A GLASS tube, one end of which is blown out to a bulb is bent around twice, as indicated in Fig. 1, and is provided with a side tube *T*. Some mercury is poured into it, which cuts off a volume of air in bulb *A*. The smaller tube *I* fitting loosely in the wider tube, is connected with the latter by a piece of rubber tubing, which at the same time allows an up and down

<sup>1</sup> Read before the New York Section, April 10th, 1896.

movement of the small tube. This apparatus is put into the air or water bath, which is to be kept at a constant temperature; its working is effected by the expansion by heat of the

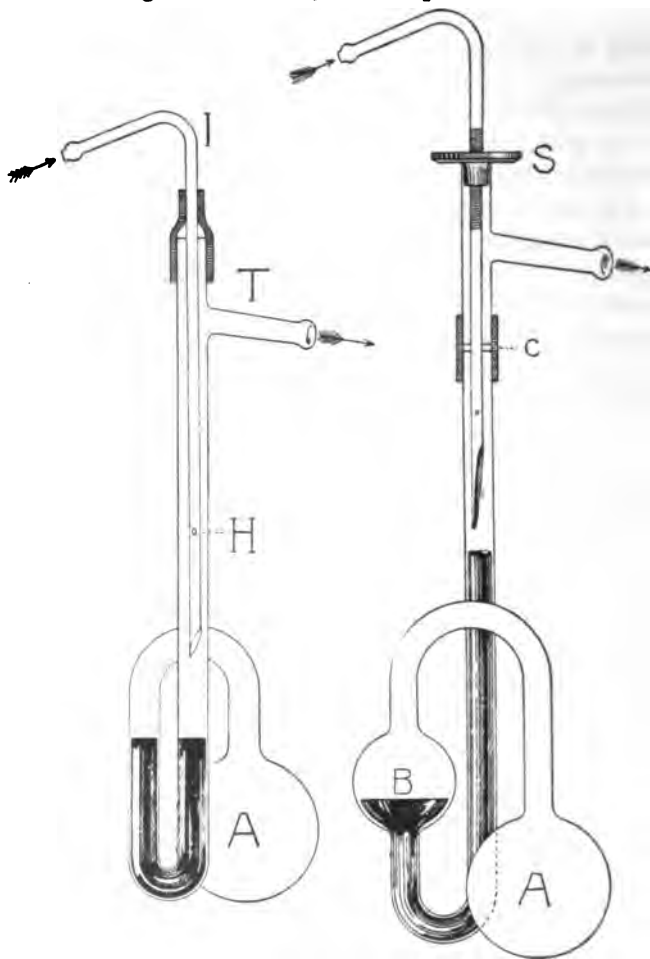


Fig. 1.

Fig 2.

volume of air in bulb *A*, which causes the mercury column to rise until it reaches pipe *I*, serving as inlet of the gas. From the space over the mercury column, the gas is conducted through the pipe *T* to the burner. As the inlet pipe is cut off

obliquely or drawn out to a slit, the supply of gas is with increased temperature diminished by and by, and might even be cut off altogether if the pipe were not provided with a small hole *H*, which allows the passage of a sufficient amount of gas to prevent the extinction of the flame. The smaller supply of gas lowers the temperature, and the sinking of the column of mercury caused thereby allows then the gas to pass again freely. It is easy to keep the air- or water-bath, which is provided with this apparatus, constantly at any desired temperature within 1° to 2° F. by regulating the position of the inlet pipe. The daily changes in the atmospheric pressure have very slight influence.

As the amount of mercury might at higher temperature not be sufficient to keep back the expanded air a small bulb might be blown in the second bend (*B*, Fig. 2), and thereby a sufficient supply of mercury for even very high temperatures can be provided. If the apparatus is intended for a closed bath, the main pipe is cut at *C*, the lower part is then fixed from inside and connected outside with the upper part by means of rubber tube. The standpipe *I* may also be regulated by a screw movement *S*.

This apparatus has the advantage of being simple and cheap. It can be used for open or closed baths at either high or low temperatures. The main drawback of all other similar apparatus is the black mass caused by the action of illuminating gas on the mercury, which collects in a short while on the surface of the mercury column and stops the action completely. The apparatus described allows the removal of the dirty mercury and filling anew in the easiest and most rapid manner.

Furthermore, there is no stop-cock or rubber tube connection between the working parts, that is, the expanded volume of air and the column of mercury.

# A RAPID METHOD OF DETERMINING THE MOLECULAR MASSES OF LIQUIDS BY MEANS OF THEIR SURFACE TENSIONS.

BY C. E. LINDBARGER.

Received May 13, 1896.

## INTRODUCTORY.

UNTIL within the last few years our knowledge of the molecular condition of liquids was very limited. Such facts as the existence of allotropic modifications of elements and of isomorphous forms of compounds, the rotation of the plane of polarized light, the abnormal vapor-densities of certain substances in the vicinities of their boiling points seemed to indicate that in liquids two or more gaseous molecules coalesce to form complex molecular groupings.<sup>1</sup> Indeed, de Heen<sup>2</sup> developed a theory of liquids on the hypothesis that liquid molecules are made up of a number of gaseous molecules, thus making a distinction between "liquidogenic" and "gasogenic" molecules. On the other hand, it has been assumed by some that the differences between gases and liquids are due solely to the greater propinquity of the molecules in the liquid condition, no polymerization of the gaseous molecules taking place. But nothing really definite about the question was advanced until Guye,<sup>3</sup> in studying the relation of his critical coefficient to the molecular mass of a liquid at its critical point, found that it was necessary to double the molecular masses of methyl alcohol and water in order to make them conform to the general rule he had established. This is the first time that a definite numerical value was assigned to the molecular mass of a liquid, and it was thereby rendered evident that both of the above suppositions in regard to the molecular condition of liquids correspond to fact; some liquids are polymerized and some are not.

<sup>1</sup> Naumann: *Ann. Chem. (Liebig)*, 155, 325, 1870; Henry: *Ann. de la Soc. Scientifique de Bruxelles*, 1878-1879, 267; Spring: *Bull. de l'Acad. de Belgique* [3], 11, No. 5, 1886; Dupré: *Théorie mécanique de la chaleur*, 147; Amagat: *Ann. chim. phys.* [5], 11, 536; Ramsay: *Proc. Roy. Soc.*, 1880, April 22 and December 16; Ramsay and Young: *Proc. Roy. Soc.*, 1885, Nov. 19, and *Phil. Mag.*, 1887, 129.

<sup>2</sup> de Heen: *Ann. chim. phys.* [6], 5, May, 1885, and *Physique Comparée et la Théorie de Liquides*, 1888.

<sup>3</sup> *Ann. chim. phys.* [6], 21, Oct. 1890; *Compt. rend.*, 110, 141 and 1128, 1890; *Bull. Soc. Chim.* [3], 3, 51; *Arch. de Genève*. [3], 23, 197; Thesis: *Le coefficient critique et la détermination du poids moléculaire au point critique*. Paris, 1891.

The next stage in the investigation of the subject was naturally the determination of the classes of liquids that are made up of simple molecules and of the classes of liquids that consist of complex molecules, or, in other words, the determination of which liquids are "normal" and which are "associated;" also the question as to the amount of association presented itself.

This investigation was taken up by Ramsay and Shields,<sup>1</sup> who, by the application of a method based upon determinations of surface energies, examined more than fifty liquids; this work may justly be considered classic and is the source of most of our definite knowledge of the size of liquid molecules.

The division of liquids into two classes according to their molecular polymerization having thus been rendered familiar and definite by the work of these two English chemists, many properties of liquids were subjected to examination in order to ascertain whether they might reveal any indications of molecular polymerization. Guye<sup>2</sup> has been particularly active in this direction; thus, he found evidence of molecular association in certain liquids, as shown by their latent heats of vaporization attaining a maximum, their curves of vapor-tensions intersecting one another, etc. Also, Linebarger,<sup>3</sup> in examining Pictet's Law (commonly but erroneously known as Trouton's Law) and in determining the specific gravities, viscosities, and other physical properties of mixtures of liquids found that certain abnormalities could be best accounted for by the assumption of the presence of polymerized molecules. Moreover, in studying the vapor-tensions of mixtures of volatile liquids, Linebarger<sup>4</sup> was led to the discovery of a method of determining the absolute molecular mass of a liquid at a definite temperature, Ramsay and Shield's method giving only the average molecular mass throughout a certain range of temperature.

Mention must also be made of an extremely simple method proposed by Traube<sup>5</sup> for ascertaining whether the molecules of a liquid are in a state of association or not; it is based upon a

<sup>1</sup> *J. Chem. Soc.*, 63, 1089, 1893, and *Ztschr. phys. chem.*, 12, 433, 1893.

<sup>2</sup> *Arch. de Genève* [3], Jan., Feb., and May, 1895; *Bull. Soc. Chim.*, 13, 34, 1895.

<sup>3</sup> *Am. J. Sci.*, 49, 381, 1895; *Am. Chem. J.*, 18, 429.

<sup>4</sup> *J. Am. Chem. Soc.*, 17, 615 and 690, 1895.

<sup>5</sup> *Ber. d. chem. Ges.*, 1894-1896.

determination of the density of the liquid under investigation.

The discovery of a method of determining the molecular masses of liquids opens up a broad field of investigation. The discoverer of a new liquid ought no longer to be content with a determination of its vapor-density or cryoscopic behavior in order to ascertain its molecular mass in the gaseous or dissolved state; he ought also to determine its surface tension, its density, or its vapor-tension in solution in order to ascertain whether it is associated or not. The method of vapor-tensions in solution, although it is the only one as yet devised that gives indications of the exact size of a liquid molecule at a given temperature, is rather long and is restricted to volatile liquids capable of analysis in the presence of the solvent. The chemist is therefore confined to the methods by Ramsay and Shields, or Traube. As stated above, Traube's method depends simply upon a determination of density; it does not seem to have attracted much attention, probably because it has merely an empirical basis. But a density determination is also required in Ramsay and Shields' method, so that the two methods may be employed together, the one serving as a control of the other.

The method of determination of molecular masses of liquids from their surface energies, as carried out with the apparatus used by Ramsay and Shields, does not seem to have been generally introduced into laboratories of organic chemistry for the probable reason that it requires careful and skillful manipulation and considerable time. There appears to be a need for an apparatus that can be handled rapidly, does not require much skill in using, is always ready for work, and gives reliable results. It is believed that the apparatus to be described in the following sections meets these requirements.

## II. DESCRIPTION OF APPARATUS.

The apparatus (Fig. 1) consists of the following pieces: A column of brass tubing *AA* with iron tripod base; a short horizontal arm *B*, to which is attached a brass gibbed plate *SS* supporting the capillary tubes by means of the clamps *CC* and *DD*, and also the micrometer screw *EF*; a retort ring *AH* bearing the beaker *II*; a compression device consisting of a screw *L*



pressing into a rubber ball *K*, which is connected by means of rubber tubing and a glass Y tube *N* to the upper extremities of the capillary tubes; a vertical rod *MM* passing through the arm *B* (to which it may be clamped by a thumb-screw not shown in the figure) and provided with rings to support the rubber tubes connected with the capillary tubes, the latter being thus relieved of the weight of the former; a test tube *O*, into which the capillary tubes pass, supported by the cover of the beaker *H*; two thermometers, one to take the temperature of the bath-liquid contained in the beaker, the other that of the liquid undergoing investigation in the test tube *O*.

Some of these pieces require a more detailed description.

The immovable part of the gibbed plate has a scale fastened along its side divided into fortieths of an inch, while its movable part has a pointer playing over this scale. Back of the gibbed plate is fixed the bearing *P*, in which the screw *EF* turns; the clamps *CC* are attached to the fixed portion of the gibbed plate, also another pointer for the milled head of the screw.

The micrometer screw demands a specially detailed description, inasmuch as the accuracy of the results obtainable by the apparatus depend mainly upon the accuracy of its construction. The one I use has forty threads to the inch, is about four inches long, and of good diameter, so as to give absolute motion, the adjustable split bearing *P* taking up all lost motion. Great pains were taken in turning it, and I have been unable to detect any irregularities in its construction; indeed, the screw furnished by the makers is even more accurate than is really necessary. The milled head *E* (about thirty-five mm. in diameter) is divided into 100 parts, thus giving a direct reading of  $\frac{1}{100}$  of an inch, and even less than that, since it is easy to estimate fractions of a division.

Three capillary tubes were employed in working with the apparatus:

*A* with a bore of about one and a half mm.

*B* " " " " " five-tenths mm.

*C* " " " " " one-tenth mm.

From the nature of the method it is not at all necessary to know the exact dimensions of the tubes; all that is required is

that the bore be approximately circular and the edges sharp. To prepare the capillary tubes, a stock of tubing is examined and tubes of the desired dimensions selected. Pieces are broken off from these tubes until it is found that the ends present plane surfaces perpendicular to the axis of the tube. If the clamps happen to be too large for the tubes, a filling of sheet lead may be employed.

The liquid serving as bath and contained in the beaker may be water or glycerin; it is heated by means of a Bunsen burner and kept in motion by means of a stirrer (not shown, however, in the figure). Besides this kind of a bath much use was made of a vapor jacket for keeping the temperature uniform during a determination. The test tube *O* was fitted into a considerably larger tube by means of a cork, through a second perforation of which passed a long glass tube acting as a condenser. On boiling liquids or mixtures of liquids in the larger tube, their vapors rise and heat the inner tube with its contents to a desired constant temperature for any length of time.

### III.—METHOD OF MAKING A DETERMINATION.

The first thing to do in using the apparatus is to get the lower extremities of the two capillary tubes at the same level. This may be accomplished in the following simple manner. A spirit-level is placed upon a piece of plate glass, which in turn is set upon the support *H* at the required height and levelled. The pointers of the side scale, as well as that of the screw head, are set at zero, the tubes allowed to rest freely upon the plate glass, and then clamped into position. While this way of fixing the tubes answers well enough for the initial adjustment of the apparatus, it is not sufficiently accurate to insure their being replaced in the same position, if, from any cause, they become displaced. Indeed, it is not at all certain that the tubes are at the same level to within 0.1 mm., when adjusted in the above manner; yet this degree of accuracy is entirely sufficient for the first adjustment, and later it will be shown how they can be gotten into the same position to within 0.01 mm.

The test tube has a mark scratched on its side, which indicates the volume of liquid that is to be taken for a determination

of its capillary constant, it having been found that differences in the distance between the surface of the liquid and the orifices of the tubes have a little influence upon the readings of the instrument.<sup>1</sup> The volume of the liquid may be as small as a couple of cubic centimeters, if a small test tube be used; generally, however, it is advisable to employ from five to ten cc. The test tube is filled with the liquid under examination to this mark and the tube suspended in the bath. The beaker is placed upon a piece of asbestos board or wire gauze set upon the retort ring, which is raised until the capillary tubes are close to the bottom of the test tube. A thermometer is introduced into the liquid, and the bath liquid stirred so as to insure uniformity of temperature.<sup>2</sup> The rapidity with which the liquid undergoing investigation takes on the temperature of the bath may be hastened by blowing bubbles up through it by compression of the air in the rubber ball *K*.

When the temperature of the liquid is the same as that of the bath, the movable tube (preferably the one with the smaller bore), is raised by turning the screw. This may be done rapidly while bubbles are being forced out of the larger tubes every second or so. At a certain point bubbles may cease to issue from the larger tube and commence to come from the smaller one, an indication that the correct adjustment has been passed. The screw is now turned very cautiously in the opposite direction until bubbles issue at about the same time from both of the tubes. The final adjustment is generally best made as follows:

The air is compressed *very slowly* until it has arrived just at the orifices of both tubes. The pressure is then not increased further, and, as a rule, it will be observed that, if the adjustment is perfect, bubbles will issue of their own accord from both the tubes in a second or so; sometimes one of the bubbles lags a little behind the other. The success of the operation depends upon the *steady and gradual* compression of the air; if this be subjected to abrupt or irregular changes of pressure, not inconsiderable errors may be committed. It is advisable to make at

<sup>1</sup> This influence is, however, but slight. Readings with ether were found to differ by only  $\frac{1}{16}$  of an inch, when the difference between the free surface of the liquid and the lower extremities of the capillary tubes differed by more than four inches.

<sup>2</sup> The mode of procedure is essentially the same when a vapor jacket is employed.

least two readings, one when the narrower tube is being lowered, the other when it is being raised; indeed, the readings can be made so rapidly that it is a good plan to take a half dozen or so, the tubes being moved alternately up and down.

#### IV.—DISCUSSION OF SOURCES OF ERROR IN APPARATUS.

In the determination of the capillary constants by means of the apparatus described in the preceding sections, measurements of three kinds have to be made, *viz.*, measurements of specific gravity, of temperature, and of the distance between the lower extremities of the capillary tubes. We pass to the discussion of the errors inherent to each.

I. The determination of the surface tensions by any of the direct methods, such as measuring the height to which liquids rise in capillary tubes, etc., cannot be said on an average to be accurate to more than one part in two thousand, and only in exceptional cases to one part in ten thousand. On the other hand the accuracy of a specific gravity determination can easily attain one part in ten thousand, and in many cases to even one part in a hundred thousand. In the formula to be communicated in the following section, it will be seen that the influence of the specific gravity upon the value of the capillary constant is not very great, so that a determination of the specific gravity to one part in two thousand is perhaps sufficiently accurate for our purposes, although it is of course better to be sure of the fourth decimal place. We may conclude then that the accuracy of a determination of the specific gravity of a liquid where surface tension is to be ascertained, may be counted perfect, if it be made to within one part in ten thousand.

II. For temperatures between  $0^{\circ}$  and  $50^{\circ}$  it is an easy matter to keep the temperature of even such a simple bath as the one given in Fig. 1 constant to within  $0.05^{\circ}$  long enough to adjust the apparatus and make several readings. By the use of the larger baths, or, better still, of vapor jackets, the temperature can be kept sufficiently uniform for the investigation at different temperatures of most liquids. As a variation of temperature amounting to  $0.1^{\circ}$  changes but little the readings of the apparatus, it may be allowed that the error committed in estimating the temperature is, for the purpose of this investigation, negligible.

III. The possible error that may be committed in the readings of the apparatus can best be judged by considering the readings themselves. A number of series of readings for different liquids at various temperatures are accordingly given just as they were taken directly from the apparatus.

The readings are not to be taken as material for the calculation of the surface tensions of the liquids, as in some cases they do not represent the true distances between the lower extremities of the capillary tubes, the positions of these having been altered purposely several times. The unit of a reading is a fortieth of an inch.

Nitroethane<sup>1</sup> at 16.95°. Tubes A and B.

23.27  
23.26  
23.28

Nitroethane<sup>1</sup> at 46.6°. Tubes A and B.

21.23  
21.26  
21.21

Nitromethane<sup>1</sup> at 24.5°. Tubes A and B.

24.28  
24.26  
24.23  
24.25  
24.29  
24.26  
24.26

Nitromethane<sup>1</sup> at 41.5°. Tubes A and B.

22.86  
22.87  
22.80  
22.81  
22.85

Benzene at 20.0°. Tubes A and B.

22.86  
22.88  
22.85  
22.86  
22.87

Benzene at 20.5°. Tubes B and C.

30.55  
30.54  
30.59  
30.56  
30.55

Toluene at 25.0°. Tubes A and B.

24.42  
24.44  
24.41  
24.40  
24.43

Toluene at 46.6°. Tubes A and B.

22.65  
22.63  
22.62  
22.63  
22.64

Another series made ten days later.

24.43  
24.45  
24.42  
24.43  
24.45

22.64  
22.66  
22.64

<sup>1</sup> Made by Mr. L. W. Jones, of the University of Chicago.

Methyl nitrate at 0.2°. Tubes A and B.		Carbon bisulphide at 19.5°. Tubes A and B.	
	18.29		19.35
	18.28		19.32
	18.25		19.30
	18.26		19.33
	18.28		19.34
Ethyl ether at 0.1°. Tubes A and B.		Ethyl ether at 25.0°. Tubes A and B.	
	17.90		13.55
	17.92		13.53
	17.92		13.52
	17.95		13.54
	17.93	Another series made over a month later.	
			13.54
			13.55
			13.53
Toluene at 78.4°. Tubes B and C.		Monochlorbenzene at 77.8°. Tubes B and C	
	24.73		23.34
	24.77		23.38
	24.75		23.32
	24.71		23.35
	24.74		23.34
Ethyl iodide at 25.0°. Tubes A and B.		Ethyl alcohol at 51.0°. Tubes A and B.	
	8.89		18.65
	8.87		18.62
	8.88		18.64
	8.88		18.61
	8.87		18.63
Another series made twenty days later.			
	8.87		
	8.86		
	8.88		
Water at 40.0°. Tubes A and B.		Water at 20.0°. Tubes A and B.	
	77.10		76.09
	77.13		76.13
	77.14		76.10
	77.09		76.16
	77.11		76.23
	77.16		76.14
	77.13		76.16
	77.12		76.18
			76.15
		Another series made a fortnight later.	
			76.12
			76.18
			76.21
			76.19
			76.14
			76.18

These series of numbers have been taken from my note books almost at random, and are but a small portion of the number of readings I have made. They show that for most liquids differences in the readings amounting to more than  $\frac{1}{1000}$  of an inch seldom occur, and when a series of readings are made and their average taken, the error almost vanishes. Only in case of water were greater differences of readings observed; yet, since water has such a large capillary constant, the error committed is very slight. It was observed that the nearer the extremities of the capillary tubes were, and, consequently, the smaller the numerical value of the reading, the more concordant were the readings.

While the three sources of error just discussed seem to be almost negligible, there is another, inherent, not in the apparatus, but in the method, which stands seriously in the way of obtaining reliable absolute determinations of the surface tensions of liquids. This source of error lies in the determination of the "apparatus constant," which may vary from one liquid to another. A more detailed discussion of it will be given in the next section, after the way in which the "apparatus constant" is determined is described.

#### V.—CALCULATION OF RESULTS.

Having now shown the degree of accuracy attainable in the readings of the apparatus under discussion, I will pass to the consideration of the manner in which the results obtained by this indirect method may be converted into those arrived at by direct methods. As stated above, two things besides the temperature are measured in this method: (1) the specific gravity of the liquids taken, and (2) the vertical distance between the lower ends of the two capillary tubes when air under the same pressure issues in synchronous bubbles from their orifices. It is not difficult to determine the specific gravity to within  $\frac{1}{1000}$ , although an accuracy of  $\frac{1}{1000}$  is quite sufficient. The distance between the ends of the two tubes can be measured to about a hundredth of a millimeter, except in the case of water, where the degree of accuracy of measurement is only within a tenths of the same unit of length. It is now our task to pass from the data obtained from measurements of these quantities to the capillary constants measured in dynes per centimeter.

Inasmuch as our knowledge of the form of the bubbles just on the point of issuing from the orifices of the capillary tubes is not at all precise, there appears to be no immediate way of finding a relation on theoretical grounds between the data furnished by this indirect method and those given by direct methods. Jäger<sup>1</sup> obtained the relationship employed by him in the following manner: "Wie sich unsere Annahme für die Formulirung des Einflusses, welchen die Röhrenweite auf den bewussten capillaren Druck hat, als richtig erwies, so zeigt sich, wie wir später sehen werden, dass es vollständig genügt, wenn wir

$$\alpha F(s) = \alpha(1 + \beta s)^2$$

setzen, wobei  $\beta$  eine Constante bedeutet, die sich ebenfalls leicht ermitteln lässt, wenn zwei Flüssigkeiten, deren  $\alpha$  und  $s$  bekannt sind, zu Gebote stehen. Verwenden wir nämlich zu unseren Messungen stets dieselben beiden Capillarröhren, so wird für die eine Flüssigkeit die Gleichung (1)

$$\alpha(1 + \beta s)\varphi(r, r') = hs,$$

für die zweite,

$$\alpha'(1 + \beta s')\varphi(r, r') = h's',$$

somit

$$\frac{\alpha(1 + \beta s)}{\alpha'(1 + \beta s')} = \frac{hs}{h's'}.$$

Aus dieser Gleichung kann der Werth von  $\beta$  ermittelt werden da alle übrigen in ihr vorkommenden Grössen bekannt sind."

In order to obtain the value of  $\beta$ , he made use of Brauner's<sup>2</sup> and Wolf's<sup>3</sup> directly determined data for water and ethyl ether. By transforming the immediately preceding equation into

$$\alpha = \frac{\alpha'hs(1 + \beta s')}{h's'(1 + \beta s)},$$

he obtained therefrom on putting

$$\frac{\alpha'(1 + \beta s')}{h's'} = c,$$

$$\alpha = c \frac{hs}{1 + \beta s};$$

<sup>1</sup> *Loc. cit.*

<sup>2</sup>  $a$  = capillary constant;  $s$  = specific gravity.

<sup>3</sup> *Ann. der Phys. Pogg.*, 70, 515.

<sup>4</sup> *Ann. der Phys. Pogg.*, 70, 575.



and substituting for specific gravity =  $s$ , the specific volume =  $v = \frac{1}{s}$ , he finally obtained

$$\alpha = c \frac{h}{v + \beta},$$

an equation used throughout his work in transforming his results.

It is hardly necessary to mention that the degree of accuracy that can be attributed to an indirect method of measuring a physical constant of Nature depends upon the accuracy of the results obtained by direct methods; hence the importance of choosing the most exact directly determined data for the calibration of an indirect method. Ramsay and Shields<sup>1</sup> have elaborated the method of measuring the heights to which liquids rise in capillary tubes, and have carried out series of determinations of the capillary constants of various liquids in contact only with their own vapor and glass, which are justly regarded as of the greatest trustworthiness, and may be confidently taken as standards.

If Jägers equation,

$$\frac{\alpha(1 + \beta s)}{\alpha'(1 + \beta s')} = \frac{hs}{h's'},$$

be correct, it ought to be possible to obtain the same value of  $\beta$ , when the data for  $\alpha$  and  $\alpha'$ ,  $s$  and  $s'$ , and  $h$  and  $h'$  are taken for any pair of liquids. On carrying out the calculations, however, I found, on employing the data given by Ramsay and Shields,<sup>2</sup> for the specific gravities and capillary constants, and the readings of my apparatus for the differences of level between the extremities of the two capillary tubes, that the values of  $\beta$  varied considerably for different pairs of liquids. Furthermore, it was found that, if  $\beta$  and  $c$  be calculated for any two liquids, and then from the equation

$$\alpha = c \frac{hs}{1 + \beta s},$$

the value of  $\alpha$  be deduced for a third liquid, differences between the values thus obtained and those given by Ramsay and Shields amounting to five or ten per cent. were obtained in some cases,

<sup>1</sup> *Ztschr. phys. Chem.*, 12, 433, 1895.

<sup>2</sup> *Loc. cit.*

although once in a while a pretty good correspondence was observed. Jäger's equation appears to be merely approximate and does not stand a rigid scrutiny. Jäger himself seems to find the justification of his formula in its yielding results corroborative of certain theoretical views he advances, and in the agreement between his observed values and those calculated for the same temperatures, by means of temperature coefficients; but as the temperature coefficients were derived from his own data, which differ but rarely more than five or ten per cent. from those communicated by Ramsay and Shields,<sup>1</sup> and he does not attain to a much closer correspondence than that between his observed and calculated values, the correctness of the formula does not seem to be any the better established.

It accordingly became peremptory to devise another formula which should be in better accordance with Ramsay and Shields' measurements. But here a difficulty arose. Ramsay and Shields determined the capillary constants of liquids that had been freed from air; the liquids were in contact only with their own vapor and glass. There is no doubt but that the surface tensions of liquids can be measured accurately by means of their rise in capillary tubes only when no air is present; R. Schiff<sup>2</sup> had already made this observation before Ramsay and Shields. Just what influence the presence of air has upon the capillarity of liquids we do not know; the greater or less volatility of a liquid makes the degree of dilution of air in contact with its surface correspondingly greater or less. In the apparatus described in this article, the liquid under examination is saturated with air, and the pressure of the air varies with the specific gravity of the liquid. The difficulty at issue lies in the question as to whether the indirect determinations made with liquids in contact with air are comparable to more than a gross approximation with those obtained by the direct method as employed by Ramsay and Shields. This difficulty seemed at first to be unsurmountable, but, finally, a simple relation was discovered which shows an excellent correspondence between Ramsay and Shields' data and mine.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Ann. Chem. (Liebig)*, 233, 47.

The relation in question is

$$\gamma = chs + s^2 \dots \dots (A)$$

wherein  $\gamma$  represents the capillary constant in dynes per centimeter,  $c$  the "apparatus constant,"  $h$  the distance between the ends of the tubes, and  $s$  the specific gravity. The value of the constant was obtained in the following way. The data for  $\gamma$  and  $s$  were taken from Ramsay and Shields' and Ramsay and Aston's papers, and those for  $h$  from my own measurements. These were set in equation (A) and the value of  $c$  calculated therefrom. The greatest pains were taken in the purification of the liquids examined, so that they had no doubt the same properties as those used by the investigators just named. The data and results of the calculations are given in Table I. for the tubes  $A$  and  $B$ , and in Table II. for tubes  $B$  and  $C$ .

TABLE I.

*Values of "Apparatus Constant" for Tubes A and B.*

Name of liquids.	$T$ .	$s$ .	$\gamma$ .	$h$ .	$c$ .
Water .....	20.0°	0.9984	70.72	55.60	1.248
" .....	30.0°	0.9958	69.10	54.85	1.247
" .....	40.0°	0.9923	67.50	53.90	1.245
Methyl alcohol...	20.0°	0.7905	23.03	23.16	1.227
Ethyl " ...	20.0°	0.7900	22.03	21.97	1.236
Acetone .....	16.8°	0.7798	23.35	22.95	1.238
" .....	46.4°	0.7656	19.68	20.00	1.250
Ethyl ether.....	20.0°	0.7143	16.49	17.91	1.245
" " .....	30.0°	0.7000	15.27	16.87	1.252
Ethyl iodide.....	19.1°	1.937	30.00	10.88	1.248
Carbon bisulphide	9.7°	1.2773	32.73	19.90	1.224
Benzene.....	11.2°	0.8871	29.21	25.86	1.239
" .....	46.0°	0.8500	24.71	22.75	1.241
Chlorbenzene.....	9.5°	1.1182	33.71	23.46	1.238
" .....	45.6°	1.0795	29.30	21.25	1.227
Toluene .....	15.2°	0.8682	28.18	25.21	1.253
" .....	46.6°	0.8380	24.60	22.65	1.259

Average = 1.243

TABLE II.

*Values of "Apparatus Constant" for Tubes B and C.*

Names of liquids.	T.	s.	$\gamma$ .	h.	c.
Acetone .....	16.8°	0.7998	23.25	27.72	1.023
" .....	46.4°	0.7656	19.68	24.22	1.029
Chlorbenzene.....	45.6°	1.0795	29.30	25.71	1.014
" .....	77.8°	1.0444	24.65	23.38	1.011
Ethyl ether .....	20.0°	0.7143	16.49	22.08	1.036
Benzene .....	11.2°	0.8871	29.21	31.44	1.019
" .....	46.0°	0.8500	24.71	27.86	1.013
Toluene .....	15.2°	0.8682	28.18	30.60	1.032
" .....	46.6°	0.8380	24.60	27.75	1.028
" .....	78.4°	0.8080	20.93	24.75	1.014

Average = 1.022

A glance at the tables shows that the "constants" are indeed quite constant. In Table I., the average of the numbers in the last column is 1.243; the greatest variation on one side is 0.019 for carbon bisulphide at 9.7°, and on the other side, 0.016 for toluene at 46.6°. Generally, the differences from one liquid to another are not larger than they are for the same liquid from one temperature to another. Likewise, in Table II., the average value of the constant is 1.022, with differences of 0.014 for ether at 20.0° on the one hand, and 0.011 for chlorbenzene on the other.

Introducing  $c = 1.243$  from Table I. and  $c = 1.022$  from Table II. into equation (A), and treating  $\alpha$  as the unknown quantity, I calculated the capillary constants to be those given in Tables III. and IV., respectively, beside which are placed the corresponding data given by Ramsay and Shields<sup>1</sup> and Ramsay and Ashton.

TABLE III.

*Comparison of Capillary Constants for Tubes A and B.  $c = 1.234$ .*

Names of liquids.	Temp.	$\gamma$ .	$\gamma$ .	$\gamma - \gamma$ .
		$\gamma = c h s. + s^2.$	Ramsay & Shields.	
Water.....	30.0°	68.82	69.10	-0.28
" .....	40.0°	67.42	67.50	-0.08
Methyl alcohol.....	20.0°	23.39	23.03	+0.36
Ethyl alcohol .....	20.0°	22.17	22.03	+0.14

<sup>1</sup> Loc. cit.

Names of liquids.	Temp.	$\gamma$ :	$\gamma$ .	$\gamma - \gamma$ .
		$\gamma = chs. + s^2$ .	Ramsay & Shields.	
Acetone.....	16.8°	23.34	23.35	-0.01
" .....	46.4°	19.59	19.68	-0.09
Ethyl ether .....	20.0°	16.42	16.49	-0.07
" " .....	30.0°	15.18	15.27	-0.09
Ethyl iodide .....	19.1°	29.90	30.00	-0.10
Carbon bisulphide...	9.7°	32.22	32.73	-0.49
Benzene.....	11.2°	29.31	29.21	+0.10
" .....	46.0°	24.75	24.21	+0.04
Chlorbenzene .....	9.5°	33.86	33.71	+0.15
" .....	45.6°	29.68	29.30	+0.38
Toluene.....	15.2°	27.96	28.18	-0.22
" .....	46.6°	24.25	24.60	-0.35

TABLE IV.

*Comparison of Capillary Constants for Tubes B and C.  $c = 1.022$ .*

Names of liquids.	T.	$\gamma$ .	$\gamma'$ .	$\gamma - \gamma'$ .
		$\gamma = chs + s^2$	Ramsay & Shields.	
Acetone .....	16.8°	23.32	23.35	-0.03
" .....	46.4°	19.64	19.68	-0.04
Chlorbenzene .....	45.6°	29.56	29.30	+0.26
" .....	77.8°	26.01	25.66	+0.35
Ethyl ether .....	20.0°	16.42	16.49	-0.07
Benzene.....	11.2°	29.28	29.21	+0.07
" .....	46.0°	24.88	24.71	+0.11
Toluene.....	15.2°	27.93	28.18	-0.25
" .....	46.6°	24.46	24.60	-0.14
" .....	78.4°	21.09	20.93	+0.16

It is at once apparent that only in a few instances the differences between Ramsay and Shields' results and mine amount to more than a few tenths of a per cent., and in some cases the correspondence is as good as perfect. Furthermore, the differences that are found seem to be very nearly the same when either pair of tubes is employed; this indicates that the differences are due rather to the possible differing degrees of purity in the liquids employed by each of us than to a fault in the apparatus itself. However that may be, the data show that it is possible to obtain with the apparatus in question results, which by means of the formula (A), are comparable with those obtained by Ramsay and Shields or Aston. One cannot withstand the temptation to quote Jäger's words:<sup>1</sup> "..... unsere

<sup>1</sup> *Loc. cit.*

methode is vollständig geeignet, richtige Resultate zuergeben. Fasst man noch die leichte, sichere und wenig zeit beanspruchende Handhabung, welche unser Apparat erfordert, ins Auge, so wird man wohl leicht zur Ueberzeugung gelangen, dass unter den gegenwärtigen Methoden für den praktischen Gebrauch kaum eine bessere zu finden sein dürfte." As to what pertains to the experimental handling of the apparatus, my experience with it enables me to subscribe to the above. But a restriction has to be made in regard to the conversion of the indirect results into direct ones. Jäger's formula has been shown above to be only approximately correct, and the one I propose has but an empirical basis. Although it has been found to stand the test of comparison with ten liquids of different properties, when two sets of tubes were employed, it is not allowable to claim that it will furnish reliable results for any liquid whatsoever. In other words, the instrument cannot be depended upon to give absolute data, since the "apparatus constant" may differ from liquid to liquid. Still it is not at all probable that the variations in the value of the "apparatus constant" will be very great in any case, and, as a variation of as much as ten per cent. has but a relatively small influence upon the surface tension, the method may be considered to give results accurate enough for the calculation of molecular masses, since Ramsay and Shields do not claim for their method an accuracy of more than six or seven per cent.

#### VI. MODE OF PROCEDURE IN DETERMINING THE MOLECULAR MASSES OF LIQUIDS.

In determining the molecular mass of a liquid it is well to measure its surface-tension at three different temperatures, and for this purpose vapor jackets will be found convenient. Temperatures easy to get are (1) that of the atmosphere  $10^{\circ}$  to  $25^{\circ}$ ; (2) that of boiling carbon bisulphide, about  $46^{\circ}$ ; (3) that of boiling alcohol, about  $78^{\circ}$ . Of course, other liquids than these may be used, all that is required is that the temperatures obtained are  $20^{\circ}$ - $30^{\circ}$  apart.

The liquid is placed in the test tube *O*, and carbon bisulphide is poured into the jacketing tube. The capillary tubes are im-

mersed in the liquid, and, after the temperature has become uniform, several readings are made, their average being taken. The carbon bisulphide is now boiled and when the temperature has become constant a second series of readings is made. The flame is removed and, after the liquid has cooled down a little, alcohol is substituted for the carbon bisulphide. The alcohol is now boiled and a third series of readings taken when the temperature becomes stationary. All of these operations can be easily made in less than an hour.

It is possible to determine the specific gravity of the liquid at the different temperatures during the above operation, as the capillary apparatus requires but little continuous attention, most of the time taken up in a determination being needed in warming the liquid to a constant temperature. Any of the ordinary methods of density determinations may be employed which can give it to the third or fourth decimal place.

The necessary calculations may be illustrated by a couple of examples, one of a normal liquid, the other of an associated liquid. For the theoretical grounding and fuller explanation of the method, reference must be had to Ramsay and Shields' paper.<sup>1</sup>

#### BENZENE.

$$\gamma = chs + s^2 = (1.243 \times 25.86 \times 0.8871) + 0.80 = 29.31 \text{ dynes at } 11.2^\circ.$$

$$= (1.243 \times 22.75 \times 0.85) + 0.72 = 24.75 \text{ dynes at } 46.0^\circ.$$

$$\gamma(Mv)^{\frac{1}{2}} = (78/0.8871)^{\frac{1}{2}} \times 29.31 = 575.1 \text{ ergs at } 11.2^\circ.$$

$$(78/0.8500)^{\frac{1}{2}} \times 24.75 = 501.8 \text{ " " } 46.0^\circ.$$

$$\frac{d[\gamma(Mv)^{\frac{1}{2}}]}{dt} = \frac{575.1 - 501.8}{46.0 - 11.2} = \frac{73.3}{34.8} = 2.106.$$

The value assigned to the constant by Ramsay and Shields is 2.121, from which the constant just calculated differs by only 0.015; hence benzene is a normal liquid.

<sup>1</sup> *Loc. cit.*

## ACETONE.

$$\gamma = chs + s^2 = (1.022 \times 27.75 \times 0.7998) + 0.64 = 23.32 \text{ dynes at } 16.8^\circ.$$

$$(1.022 \times 24.22 \times 0.7656) + 0.59 = 19.55 \text{ dynes at } 46.4^\circ.$$

$$\gamma(Mv)^{\frac{1}{2}} = (58/0.7998)^{\frac{1}{2}} \times 23.32 = 406.1 \text{ ergs at } 16.8^\circ.$$

$$(58/0.7656)^{\frac{1}{2}} \times 19.55 = 351.6 \text{ " " } 46.4^\circ.$$

$$\frac{d[\gamma(Mv)^{\frac{1}{2}}]}{dt} = \frac{406.1 - 351.6}{46.4 - 16.8} = \frac{44.5}{29.6} = 1.840.$$

The smallness of this constant indicates association in acetone. To determine the amount of association, we multiply the molecular mass  $M$ , by a factor  $x$ , which represents the average number of simple molecules that have coalesced to form a complex molecule. The calculation is as follows:

$$\left(\frac{2.121}{1.840}\right)^{\frac{1}{2}} = 1.25 \text{ between } 16.8^\circ \text{ and } 46.4^\circ.$$

the average molecular mass throughout this range of temperature is accordingly  $1.25 \times 58 = 73$ .

The apparatus described above was made by Walmsly, Fuller & Co., of Chicago, and has proven satisfactory in every detail. The makers inform me that they are ready to furnish the apparatus provided with a micrometer screw divided according to the metric as well as the English system.

## ON THE REACTION BETWEEN CARBON TETRACHLORIDE AND THE OXIDES OF NIOBIUM AND TANTALUM.

BY M. DELAFONTAINE AND C. E. LINEBARGER.

Received April 20, 1896.

EUG. DEMARCA<sup>1</sup> states that if the vapor of carbon tetrachloride be passed over the oxide of niobium or of tantalum heated below redness, the metallic oxides are converted into chlorides. "Dans le cas de l'acide niobique, la réaction se produit déjà, bien qu'avec lenteur à la température de la naphthalene bouillante (280°) et avec une extrême rapidité à 440°."<sup>2</sup>

Now the chlorides of these rare elements enter into reaction

<sup>1</sup> *Compt. Rend.*, 104, 111, 1887.

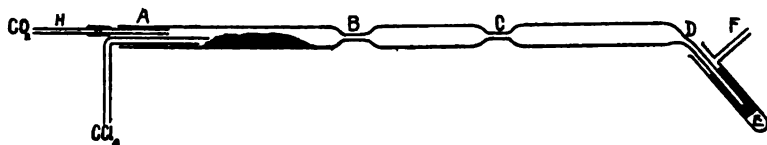
<sup>2</sup> *Loc. cit.*



very readily, and may serve as the starting points for numerous syntheses. Demarcay's statements led us to believe that the reaction in question would furnish a rapid method of obtaining these chlorides in quantity with comparative ease. On making use of the method, however, we found that the reaction does not take place in just the way indicated by Demarcay. We will first communicate our results obtained with niobic acid.

We used niobic pentoxide obtained from recrystallized potassium oxyfluosalt resulting from treatments of samarskite. The salt was decomposed in the usual way by sulphuric acid, boiled with water, and the residue ignited at strong red heat to expel the last traces of sulphuric acid.

The oxide was placed in one end of a piece of hard glass tubing, constricted in several places (Fig. 1), and the tube was heated in the vicinity of the oxide in a combustion furnace to



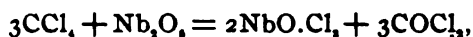
300°-400°. When the vapor of carbon tetrachloride was passed over the heated oxide, a reaction occurred immediately, and a yellowish white sublimate condensed in the cooler parts of the tube. If the oxide employed was quite pure, almost the totality of it could be converted into the volatile product. By careful application of heat it was possible to drive the sublimed substance into the further portions of the tube; it was then seen that the sublimate could be separated into two main portions, a more volatile one of a yellow color, and a less volatile one of a nearly white color. The properties of the yellow product were those of the pentachloride of niobium, while the properties of the whitish portion agreed with those of the oxychloride of niobium. By far the larger portion of the product of the reaction consisted of the oxychloride. The action of carbon tetrachloride on niobic acid seems to yield principally the oxychloride of niobium as the solid product; of the gaseous products formed, phosgene seemed to predominate.

It was thought that possibly the presence of even a slight

amount of air might exercise an oxidizing influence upon the pentachloride at the moment of its formation, converting it into the oxychloride. We accordingly carried out the same experiment in an atmosphere of carbon dioxide, but could not see that the proportion of the pentachloride was at all increased.

Again it was considered that the relative amount of the pentachloride might be made greater by allowing the reaction to take place in an atmosphere of chlorine, but even under such conditions the principal product was found to be the oxychloride.

We conceive then that the main reaction of carbon tetrachloride and niobic pentoxide may be represented by the equation



which illustrates again the tendency that niobium has to enter into combination as *niobyl*.

We have prepared a considerable quantity of niobyl chloride according to the above reaction, and, after numerous experiments, have adopted the following method of conducting the operation :

A tube of the shape indicated in the figure is prepared and filled with niobic pentoxide between *A* and *B*. As the chlorine compounds of niobium are quite voluminous, care has to be taken not to employ too much of the oxide; we found that for a tube of about two cm. bore and having a length of about forty cm. between *A* and *B*, ten to fifteen grams could be taken. The tube is placed in a combustion furnace and the portion in the vicinity of the oxide heated to about 400°. A current of dry carbon dioxide is now passed through the tube to dry it thoroughly and expel the air. The constrictions at *B* and *C* are heated nearly to redness to prevent their becoming stopped up, and carbon tetrachloride is gently distilled over upon the niobium compound. It is advisable to discontinue the current of carbonic acid by pinching the delivery tube together at *H*, since often the pressure of the tube becomes sufficient to throw the acid out of the generator. In the early stages of the operation, there occurs a transportation of substance in such a fine state of division that it is carried clear through the tube; in

order to prevent its entering the wash bottle containing sulphuric acid, and connected at *F*, a little glass wool or asbestos fiber is packed around the end of the tube in *E*. When *BC* becomes nearly filled with the products of the reaction, it is heated to a temperature just sufficient to volatilize the pentachloride, which may then be driven over into *CD*, leaving almost pure oxychloride in *BC*. When the reaction is at an end, no more carbon tetrachloride is passed into the tube, but the current of carbon dioxide is again sent through it in order to aid in the separation of the pentachloride from the oxychloride of niobium. Any carbon tetrachloride that may have condensed in *CD* is driven over into *E*, and *BC* and *CD* are so heated that the pentachloride passes through the constriction *C* and condenses just in front of *D*. While it is possible to drive almost all of the pentachloride out of *BC* and thus to obtain almost pure oxychloride, there is always a not inconsiderable portion of the latter compound that finds its way into *CD*.

In several experiments we found that a small quantity of an orange-colored sublimate collected at the further end of *CD*, which circumstance proves that this substance is more volatile than the pentachloride of niobium. H. Rose<sup>1</sup> also observed the formation of such a colored product when he was engaged in the investigation of chlorine on an intimate mixture of charcoal and tantalic acid. He found that if the acid employed contained "nur die geringste Spur von Wolframsäure, so zeigt sich bei der Darstellung des Chlorids eine sehr kleine Menge von einem rothem Chloride, das etwas flüchtiger als das Tantatchlorid ist." The compound is probably the oxytetrachloride of tungsten, its formation being due to a slight contamination of our niobic acid with a tungsten compound.

When we passed the vapor of tetrachloride over tantalic acid, no reaction took place at a lower temperature than 400°, when a small amount of volatile substance was formed, which soon ceased, however. Even on heating to a temperature high enough to cause the Bohemian glass tube to soften, we did not obtain any more of the sublimable product. The tantalic oxid turned yellow and assumed a pasty condition. It is probable that the

<sup>1</sup> *Ann. chem. phys.*, Pogg., 99, 75, 1856.

sublimed substance consisted of the chlorine compounds of niobium, since it is quite possible that our tantalic oxid was not entirely free from an admixture of niobic oxid. This behavior suggests a method of purification of tantalic acid containing a little niobic acid; we will not lay much stress on this, however, until we have done more work on the subject.

The readiness with which niobium oxychloride was formed in all our experiments contrasting with the comparatively small quantity of the pentachloride obtained illustrates once again the great inclination niobium has to enter into combination not as an individual element, but in the form of the radical *niobyl*. The action of sulphur and chlorine on  $\text{NbO}$ , investigated by Delafontaine, the numerous series of oxyfluor-salts prepared by Marignac, and the decomposition of niobyl chloride by magnesium are other facts of the same import. In this respect the analogy of niobium and vanadium is very striking, but it is almost entirely lacking in niobium and tantalum.

## THE CHEMICAL NATURE OF DIASTASE.<sup>1</sup>

### SECOND PAPER.

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received May 15, 1896.

In a former paper, by one of us,<sup>2</sup> the results of some attempts to isolate diastase have been detailed. This work has been continued, but as yet no preparations of diastase have been realized more active than those there described. The results given in the former paper, however, have been confirmed, and details of the process for obtaining highly active diastase have been determined more exactly.

Here follows a concise account of this later work so far as it is worth placing on record.

Fifteen kilograms of fine ground malt were treated with thirty liters of five per cent. sodium chloride brine, and after standing some time, with frequent stirring, the extract was pressed out and filtered, yielding sixteen liters of clear filtrate. The meal residue was again treated with fifteen liters of five per cent. brine

<sup>1</sup> From the Report of the Connecticut Agricultural Experiment Station for 1895.

<sup>2</sup> Eighteenth Annual Report of this Station, pp. 192-207; *J. Am. Chem. Soc.*, 17, 587-603.

and fifteen liters more of clear extract obtained. The united solutions were then saturated with ammonium sulphate and the precipitate filtered out, dissolved in brine and filtered perfectly clear. This liquid was saturated with ammonium sulphate, the precipitate was suspended in two liters of water and dialyzed two days. The ammonium sulphate which adhered to the precipitate, at first prevented solution of the substance, but after two days enough sulphate was removed by dialysis to allow the proteid to dissolve. The solution was filtered clear and dialyzed seven days longer. The globulin thus precipitated was filtered out and the solution, which measured 5800 cc., was dialyzed into an equal volume of alcohol of 0.86 sp. gr. for eighteen hours. The precipitate, VI,<sup>1</sup> was filtered out and the solution, which then measured 3500 cc., was again dialyzed into an equal volume of alcohol of 0.86 sp. gr. for eighteen hours yielding precipitate VII. The filtrate from VII measured 2700 cc. and was dialyzed into an equal volume of alcohol of 0.86 sp. gr. for eighteen hours, giving precipitate VIII, the filtrate from which measured 2000 cc. and was dialyzed into 2500 cc. of alcohol of 0.82 sp. gr. for eighteen hours. This gave precipitate IX, the filtrate from which measuring 1800 cc. was dialyzed into twice its volume of alcohol of 0.81 sp. gr., giving precipitate X. The solution filtered from X was then treated with absolute alcohol until nothing further separated, giving precipitate XI.

These six fractions were all, separately, treated with water; X and XI dissolved completely, the others partially. The aqueous solutions, filtered clear, containing the proteoses and albumin of the six fractions, were then separately dialyzed into water, to remove all freely diffusible substances and, as no globulin was precipitated from any of them, the dialyzers were transferred to alcohol, in order to concentrate their contents, and absolute alcohol was finally added until the proteids were completely thrown down.

In this way six preparations were obtained, which, when dehydrated with absolute alcohol and dried over sulphuric acid, weighed respectively, 18, 1.37 gram; 19, 1.47 gram; 20, 4.05

<sup>1</sup>The precipitates and preparations described in this paper are numbered consecutively with those specified in the former article on Diastase: This Journal. 17. 587.

grams; 21, 4.82 grams; 22, 2.17 grams; and 23, 0.63 gram.

The diastatic power of these preparations was determined in the manner described in the former paper,<sup>1</sup> and found to be as follows: 18 = 0; 19 = 60; 20 = 300; 21 = 300; 22, trace, and 23 = 0.

It will be noticed that nearly all the enzyme was thrown down in fractions 8 and 9, which gave preparations 20 and 21. These were but half as active as preparation 15, described in the former paper.

In order to purify this diastase, 20 and 21 were united, dissolved in 100 cc. of water, the insoluble matter filtered out and washed with thirty-five cc. of water (these first washings being added to the filtrate), then with more water, and finally with absolute alcohol. Dried over sulphuric acid, this preparation, 24, weighed 0.23 gram. The filtrate and first washings from 24 were treated with 200 cc. of alcohol of 0.885 sp. gr., making a solution containing 36.5 per cent. of alcohol. A small precipitate resulted, 25, which when filtered out and dried over sulphuric acid, weighed 0.25 gram, and had a diastatic value of 15. The filtrate from this precipitate was mixed with 160 cc. of alcohol of 0.84 sp. gr., raising the per cent. of alcohol to 50.7, and the precipitate, 26, thus produced when dried as usual weighed 2.35 gram and had a diastatic value of 86. To the filtrate from 26, 100 cc. of alcohol of 0.84 sp. gr. and 100 cc. of absolute alcohol were added, raising the alcohol-content to 61.6 per cent. The precipitate, 27, which resulted, was filtered out, weighed 2.87 grams and had a diastatic value of 600, just twice that of 20 and 21, from which it had been derived, and just equal to that of the most active preparation, 15, of the former paper. To the filtrate 200 cc. of absolute alcohol were added, giving a precipitate, 28, which weighed 1.00 gram and had a diastatic value of 100.

The filtrate from 28 mixed with 200 cc. more of absolute alcohol, gave a precipitate, 29, which weighed 0.40 gram and showed only a trace of diastatic power. The filtrate from 29, mixed with 400 cc. of absolute alcohol, yielded 0.17 gram of substance, 30, that was totally inactive, and the filtrate from

<sup>1</sup> Report of Conn. Expt. Station for 1894, p. 194; *J. Am. Chem. Soc.*, 17, 587.

this when evaporated to dryness left a residue weighing 0.65 gram.

The results of this experiment showed that little diastase was precipitated by bringing the alcohol-content of the malt extract to fifty per cent. by weight, while nearly all the diastase was thrown down, under the conditions described, when the proportion of alcohol in the malt extract was made sixty per cent.

In order to still further concentrate or purify the diastase contained in precipitate 27, this was treated with 100 cc. of water and, without filtering from the substance which had been coagulated by precipitation and drying, 100 grams of absolute alcohol were added. The precipitate so produced was filtered out and extracted with water. The insoluble matter, after washing and drying, weighed 0.50 gram. The aqueous filtrate, from this insoluble matter, was then completely precipitated with absolute alcohol and 0.45 gram of substance, 31, obtained having a diastatic value of 200. The solution, filtered from the first precipitate, produced by adding an equal weight of alcohol to the solution of 27, as just described, was mixed with enough absolute alcohol to raise this ingredient to fifty per cent., and the substance thereby thrown down, 32, weighed, when dry, one gram, and had a diastatic value of 400. The filtrate from 32 was completely precipitated with absolute alcohol and yielded two-tenths gram of inactive proteid. It is thus seen that the diastase instead of increasing in power under this treatment declined to two-thirds of its original in activity.

Having thus learned more exactly the conditions under which diastase may be so far separated from the other malt proteids, an attempt was made to prepare a large quantity of material with which to carry the purification farther. Through the kindness of Mr. C. Von Eggloffstein, of the Maltine Manufacturing Company, at Yonkers, N. Y., a considerable supply of malt extract, rich in diastase, was placed at our disposal. For this favor and much information respecting malt extracts, we wish to express our especial thanks.

One gallon (3,785 cc.) of this malt extract, which had been concentrated at a low temperature *in vacuo* until it contained about fifty per cent. of solid matter, was dialyzed into water for

forty-eight hours, whereby a large part of the sugar was removed and a thin liquid remained. This was saturated with ammonium sulphate and the precipitated proteids were filtered out, suspended in water and dialyzed for five days. To the liquid contents of the dialyzer, filtered clear from insoluble matters, alcohol was added to make fifty per cent. of the resulting mixture. This threw down a precipitate which was filtered out, dehydrated with absolute alcohol, and dried over sulphuric acid.

This white, easily-powdered precipitate, XII, weighed ninety-five grams. One-half of it was insoluble in water and salt solution. By extraction with water and precipitation with alcohol, added first to fifty per cent. and afterward to sixty per cent., two preparations, 33 and 34, resulted, weighing respectively 4.85 grams and 7.21 grams, that had little diastatic power.

The solution from which the first precipitate, XII, had been separated was treated with enough alcohol to make seventy-five per cent., and the resulting precipitate, XIII, filtered out and found to weigh, when dried over sulphuric acid, seventy grams. This precipitate included the chief part of the diastase of this extract. It dried to a light, dusty powder of pale straw yellow color, almost entirely soluble in water and had a diastatic value of 200.

XIII was dissolved in water and fractionally precipitated, but, for some unknown reason, the resulting fractions were almost entirely inactive.

In another attempt to make a large quantity of diastase, three gallons (11.4 liters) of the highly concentrated malt extract were mixed with half their weight of water and enough alcohol to make a mixture containing forty-six per cent. of alcohol. A very large precipitate, XIV, resulted, which was filtered out, and as it consisted almost entirely of insoluble matter (probably globulin), it was not further examined.

The filtrate from precipitate XIV was treated with alcohol, raising the strength to sixty per cent; the precipitate so produced was filtered out and, as it contained a large amount of sugar, it was dissolved in about five liters of water, the resulting solution was saturated with ammonium sulphate, the precipitate filtered out, suspended in one liter of water and dialyzed



for five days. The precipitate in the dialyzer was filtered out and the clear solution was treated with alcohol sufficient to make fifty per cent. of the resulting mixture, but as only a little substance separated, the amount of alcohol was increased to sixty per cent. This threw down a considerable precipitate, XV, which, when dehydrated with absolute alcohol and dried over sulphuric acid, weighed fifty-seven grams and had a diastatic value of 300.

Numerous attempts were made to obtain from portions of precipitate XV, by fractional precipitation with alcohol, diastase of greater power than 300, but without success.

Several hundred trials were made with the object to determine precisely the influence of certain conditions, such as the age of the diastase solution, and of certain substances, added in systematically varied quantities, especially sodium chloride, disodium orthophosphate, tripotassium orthophosphate, orthophosphoric acid, acetic acid, and citric acid (using the amount of copper reduction as the measure of effect), but, while the results were decisive in some cases, *e. g.*, citric acid, in the minutest quantities, always depressed or destroyed diastatic action, in the majority of instances, no such uniform results were attainable as would lead to safe conclusions in regard to the circumstances that insure a high degree of diastatic activity.

From our experience in testing these preparations it would seem that the purer the diastase is made, the more sensitive it is to external conditions, and that the method of testing the purity of the ferment by its maltose-producing power thus becomes of uncertain value and perhaps fails to furnish a safe criterion of the purity of the enzyme. That the proteid is not the only factor involved in the amylolytic action of diastase is indicated by the great influence on its activity that often accompanies the addition of various substances to its solution. In view of these facts it is not at all improbable that in thus attempting to purify diastase we remove some substance that favors, or is essential to its action, and that we may have in hand what may be properly termed the enzyme itself, which is feeble in its operation through the absence of deficiency of some accessory substance. Thus the addition of sodium chloride in

many cases increases the diastatic action several fold. That the albumin is an essential factor in diastatic action could not be positively proved, but the results of further experience have tended to strengthen this belief. Of all the preparations that we have made, none from which albumin was absent showed amylolytic power, and those containing the most albumin were the most active. It was always possible to roughly judge of the diastatic power of a preparation, by heating a portion of its solution to 65° C. and observing the amount of coagulum formed.

The fact that active diastase was obtained only from solutions whose alcohol content lies between fifty and sixty per cent., may, we think, be regarded as probable evidence that the enzyme is not something carried down mechanically with the proteid.

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### THE PROTEIDS OF MALT.<sup>1</sup>

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received May 25, 1896.

AS is well known, water extracts a considerable quantity of proteid matter from ground malt. This we find to consist of at least five distinct bodies, namely, a globulin, an albumin and three proteoses. Whether true peptones are present was not determined, for the malt extracts are so strongly colored that the biuret test entirely fails. Besides the proteids soluble in water another exists that may be taken up by dilute alcohol (of 0.9 sp. gr.). After extracting malt with saline solutions and alcohol, a further quantity of proteid matter remains, the nature of which we have not been able to determine.

*Malt-Globulin.*—Ten kilograms of air-dried malt, freshly prepared by ourselves in the laboratory, and ground to a fine meal were treated with twenty liters of water and, after standing three hours, were squeezed out in a press and the solution filtered clear. The residual meal was treated with eight liters more of water and the second solution was pressed out and filtered. The united solutions were saturated with ammonium sulphate, the precipitate was suspended in about four liters of water and dialyzed for three days, when it dissolved, with the exception of a

<sup>1</sup>From the Report of the Connecticut Agricultural Experiment Station for 1895. Communicated by the authors.

slight residue. In order to reduce its volume and separate impurities, the filtered solution was again saturated with ammonium sulphate, the precipitated substance was suspended in 1500 cubic centimeters of water and dialyzed until the greater part of the ammonium sulphate had been removed, when the solution was filtered clear. The matters now remaining undissolved were treated with ten per cent. salt solution to extract any soluble globulin which might have been deposited during dialysis, and the substance not taken up in salt-solution was filtered out. This last unquestionably consisted almost entirely of insoluble globulin, but as it separated from an unfiltered solution and was small in quantity it was not further examined. The salt-solution was then dialyzed free from chlorides, and the globulin thus precipitated was filtered out, washed with alcohol and dried over sulphuric acid. But 0.5 gram of substance was obtained which, dried at  $110^{\circ}$ , gave 0.93 per cent. of ash and, reckoned ash-free, 15.70 per cent. of nitrogen. This was marked preparation 1.

The solution of the ammonium sulphate precipitate, containing the bulk of the malt-proteid, from which the insoluble matter yielding preparation 1 had been filtered, was dialyzed, first, into water, until the salts were mostly removed, and then into an equal volume of alcohol of 0.84 sp. gr. for forty-eight hours. The proteid thus precipitated was filtered out and the filtrate was dialyzed into alcohol. After filtering out the second precipitate, the filtrate was dialyzed into stronger alcohol, and this process was repeated, thus depositing the proteids in four fractions, a fifth being obtained by adding absolute alcohol to the remaining solution as long as anything was thrown down. Each of these five fractions was then treated with water to dissolve albumins and proteoses and the resulting solutions were dialyzed in water for several days. The first four fractions were but partly soluble in water, and accordingly, the insoluble parts, after washing with water, were treated with ten per cent. sodium chloride solution, and the portion which in each case remained undissolved was filtered out, washed thoroughly with water and alcohol and dried at  $110^{\circ}$  for analysis. The four saline extracts were then dialyzed, but those from the third and fourth fractions were

found to contain only trifling quantities of proteids. That from the second fraction gave no precipitate of globulin on dialysis, but by adding alcohol to the solution 0.49 gram of preparation 2 was obtained, having 4.33 per cent. of ash and, calculated ash-free, 15.18 per cent. of nitrogen. The sodium chloride extract from the first fraction gave a precipitate on dialysis which, after washing with water and with alcohol, weighed one and two-tenths grams, 3.

The filtrate from 3, by precipitation with alcohol, yielded 4, weighing 1.54 grams.

After extracting the four fractional precipitates with water and with salt solution, the undissolved residue, in each case, was washed thoroughly with salt solution, with water and with alcohol and dried over sulphuric acid, giving, in the order named, preparation 5 weighing eight grams, 6 weighing five grams, 7 weighing 2.87 grams, and 8 weighing nine-tenths gram. These preparations, dried at 110°, had the following composition :

## MALT-GLOBULIN, BYNEDESTIN.

	3.	4.	5.	6.	7.	8.
Carbon....	53.11	53.58	53.55	53.51	53.25	53.42
Hydrogen..	6.45	6.70	7.01	6.75	....	7.15
Nitrogen..	15.78	15.86	15.87	15.72	15.87	16.12
Sulphur }	24.66	23.86	1.23	1.12	1.38	22.78
Oxygen }			22.49	22.75		
	100.00	100.00	100.00			100.00
Ash.....	0.75	1.43	1.09	0.66	0.55	0.24

Preparations 5 and 6 have the same composition as the globulin 3 and 4 obtained from the sodium chloride extracts of the fractional precipitates, while 3 contains nearly one per cent. more nitrogen, and as will be seen later, has nearly the same composition as malt albumin and is unquestionably for the most part albumin coagulated by the action of the alcohol. 7 appears to be a mixture of coagulated globulin and albumin. In a similar manner three other preparations of the coagulated globulin 9, 10 and 11 were obtained from another lot of malt.

## MALT-GLOBULIN, BYNEDESTIN.

	9	10	11
Carbon .....	52.90	52.99	53.15
Hydrogen.....	6.74	6.64	6.52
Nitrogen.....	15.33	15.31	15.81
Sulphur .....	1.17	25.06	{ 1.47 23.05
Oxygen .....	23.86		
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00
Ash .....	0.44	0.32	0.23

Preparations 9 and 10 are lower in carbon and nitrogen than those just described, probably because, having been prepared in a smaller quantity, they carried down a larger proportion of impurities when thrown out of solution by alcohol.

From a malt extract that had been concentrated *in vacuo* at a low temperature, for which we are indebted to Mr. C. von Egloffstein, alcohol, added to make forty-six per cent. by weight of the mixture, threw down a large quantity of coagulated globulin that was not further examined, the filtrate from which, on increasing the content of alcohol to sixty per cent., gave a second precipitate that was largely soluble in water. It was accordingly mixed with water and with ammonium sulphate in excess, and the substance thus thrown down was suspended in a liter of water and dialyzed for five days. The insoluble residue in the dialyzer, when washed with water and alcohol, gave preparation 12, weighing 26.78 grams. From this same extract by fractional precipitation with alcohol another small preparation of coagulated globulin, 13, was obtained.

## SUMMARY OF ANALYSES OF MALT-GLOBULIN, BYNEDESTIN.

	1	2	3	4	5	6
Carbon .....			53.11	53.58	53.55	53.51
Hydrogen ...			6.45	6.70	7.01	6.75
Nitrogen ....	15.70	15.18	15.78	15.86	15.72	15.87
Sulphur } ...			24.66	23.86	1.23	1.12
Oxygen } ...						
			<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

	9	10	11	12	13
Carbon .....	52.90	52.99	53.15	53.04	52.96
Hydrogen ...	6.74	6.64	6.52	6.57	6.83
Nitrogen ....	15.33	15.31	15.81	15.94	15.96
Sulphur } ...	1.17		1.47		
} ...		25.06			
Oxygen } ...	23.86		23.05	23.61	24.25
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

Although considerable differences exist among these analyses, they agree with each other as well perhaps as could be expected considering the difficulty of preparing the substance in a state of purity.

Whether other globulins occurred in the malt could not be determined by fractional precipitation owing to the small total quantity of globulin present.

The malt residue remaining after extracting with water, in the case first described, was treated with ten per cent. salt solution and the clear filtered liquid was dialyzed until free from chlorides. The precipitated globulin was filtered out, washed with water and alcohol and dried over sulphuric acid. This preparation, 14, weighed 4.12 grams and had the following composition :

MALT-GLOBULIN, BYNEDESTIN.

	I.	II.	Average.
Carbon .....	52.94	52.78	52.86
Hydrogen .....	6.87	6.79	6.83
Nitrogen .....	16.16	16.18	16.17
Sulphur .....	1.14		1.14
Oxygen .....			<u>23.00</u>
			100.00
Ash .....	0.96		

It is to be noted that the carbon is a little lower and the nitrogen higher than the average of the figures previously obtained. This is perhaps due to presence of a little edestin,<sup>1</sup> the globulin of ungerminated barley. Edestin is not readily soluble in dilute saline solutions, such as are formed on treating seeds with water, and, if occurring in the malt, ought to be present in the salt extract of the meal after it has been exhausted with water.

<sup>1</sup> Annual Report of Conn. Agr. Expt. Station for 1894, p. 172, and Journal of American Chemical Society, 17, 545.

Owing to the incomplete extraction with water, the preparation obtained in this case should be a mixture of the two globulins, if both are present. Edestin can only occur in extremely small quantity in malt, since but 4.12 grams of globulin were obtained by extracting ten kilograms of malt with salt solution after treatment with water, and most of this consisted of the more soluble globulin first described. It is interesting to note the practically complete disappearance of edestin during germination and the formation of the more soluble globulin with three per cent. less nitrogen and two per cent. more carbon. It is, of course, not demonstrated that the malt globulin is derived from edestin, but that the proteids undergo extensive changes before conversion into proteoses and peptones is very evident.

When dissolved in considerable quantity in salt solution, bynedestin is precipitated by water, is not precipitated by saturation with sodium chloride, and but partly by saturation with magnesium sulphate. With the biuret test it gives a violet color. Dissolved in ten per cent. sodium chloride solution and heated to 65°, a turbidity is produced which increases to flocks at 84°. The coagulum gradually augments as the temperature rises but, after heating to 100°, the filtrate from the coagulum yields an abundant precipitate on adding dilute hydrochloric acid. The solution in ten per cent. sodium chloride brine gives a precipitate with acetic acid which is soluble in an excess of the acid. These reactions show that this body is in no sense a proteose, but has characters common to plant globulins. Bynedestin formed about sixty per cent. of the total water-soluble proteid matter in the malt extract first described in this paper. Out of a total of 33.27 gram of proteid recovered in the different preparations from 10,000 grams of malt, 19.88 grams consisted of bynedestin.

*Malt Albumin, Leucosin.*—Under the name leucosin, one of us has described an albumin occurring in small quantity in the seeds of wheat, rye and barley. In the aqueous malt-extracts an albumin is found identical with leucosin in properties and composition. As stated in previous papers, this albumin is so intimately associated with diastatic action as to make probable that it is either diastase itself or an essential factor in diastatic

amylolysis. In attempts to fractionally separate malt-leucosin from the associated proteids, many preparations have been made which are mixtures of leucosin with proteose. In several cases these mixtures have been analyzed and have so nearly the composition of leucosin as to make certain that one of the proteoses of malt has very nearly the same ultimate composition as the albumin. Analyses of these mixtures may therefore be taken to represent the composition of either of these proteids.

In the extraction first described in this paper, two preparations, 15 and 16, of albumin coagulated by alcohol, were obtained from solutions out of which the globulin had been precipitated by alcohol. If, as is invariably assumed, proteose cannot be rendered insoluble by contact with alcohol, these preparations may be taken to represent the composition of malt albumin. Their composition is here compared with that of leucosin coagulated by heat.

LEUCOSIN.			Wheat, rye and barley. Average.
	Malt.		
	15	16	
Carbon.....	53.23	52.90	52.93
Hydrogen.....	6.64	6.79	6.80
Nitrogen.....	17.00	16.41	16.70
Sulphur .....	23.13	23.90	1.37
Oxygen .....			22.20
	100.00	100.00	100.00
Ash.....	0.84	0.55	

The following figures give the composition of preparations derived from three different samples of malt. These were all obtained by precipitating the proteids with ammonium sulphate, dissolving the precipitates in water, dialyzing away the greater part of the salt and fractionally precipitating the solutions with alcohol. The fractions were dissolved in water as far as possible, filtered from the undissolved globulin and the aqueous solutions dialyzed for several days in water and then in alcohol. The proteids thus precipitated were mixtures of proteose and albumin. It will be noted that they all agree fairly well with one another and with leucosin in composition. Since these mixtures contained



from six and a half to fifty per cent. of albumin, it is evident that the two proteids have a very similar composition.

## MALT LEUCOSIN AND PROTEOSE.

	17	18	19	20	21	22	23	24
Carbon.....	53.16	53.19	52.80	52.50	52.38	52.85	52.61	52.55
Hydrogen .....	7.03	6.71	6.96	6.72	6.63	6.67		
Nitrogen.....	16.50	16.60	16.09	16.10	16.51	16.25	16.35	16.41
Sulphur .....	23.31	1.38	1.45	24.68	24.48	24.23		
Oxygen .....		22.12	22.70					
	100.00	100.00	100.00	100.00	100.00	100.00		
Ash.....	0.84	0.78	0.59	0.66	1.55	0.22	0.51	

The preparations containing the most albumin, when dissolved in water, became turbid on heating to 50° and formed flocculent coagula at 58°. By saturating their solutions with magnesium sulphate the albumin was completely thrown out, and together with it much of the proteose. Saturating solutions of these preparations with sodium chloride, gave no precipitate when they contained but little albumin, but a heavy precipitate appeared on adding acetic acid to the salt-saturated solution. Solutions of the preparations containing much albumin gave precipitates on saturating with sodium chloride.

## PROTEOSES OF MALT.

The proteose associated with albumin has the properties of a *protoproteose*, since it is readily and abundantly precipitated from its salt-saturated solution on adding acetic acid.

When malt extract is fractionally precipitated with alcohol a considerable quantity of proteose is thrown down before the albumin, so that the water-soluble part of the first fraction is chiefly proteose. The proportion of albumin in the precipitates increases as the alcohol is made stronger up to the point where it is all precipitated. At this stage much proteose remains dissolved which behaves differently from that first thrown down. A large quantity of concentrated malt extract was precipitated by alcohol added to 60 per cent., and after filtering, the proportion of alcohol was raised to seventy-two per cent. The substance thereby precipitated, when dried over sulphuric acid, weighed thirty-eight grams. This was dissolved in water, the solution was heated to boiling,

the coagulated albumin was filtered out and twenty per cent. of sodium chloride added to the solution. This caused a slight precipitate which was evidently the alcohol-soluble proteid, to be described later. The filtrate from this substance was then treated with a little acetic acid, which produced a copious precipitate that was filtered out and dissolved in water. This solution, exactly neutralized with sodium carbonate and fully saturated with salt, yielded a considerable precipitate, which was filtered out, dissolved in water and dialyzed free from chlorides.

A very small deposit, consisting of minute spheroids, was found in the dialyzer. This dissolved readily in exceedingly dilute salt solution, from which it was thrown down by much water. On adding nitric acid to the solution of this substance a precipitate was produced that dissolved on warming and reappeared on cooling, gave a clear pink biuret reaction and was precipitated by copper sulphate. On boiling its solution not even a turbidity was produced. Except for its behavior on heating, this substance has all the reactions of a *heteroproteose*. The amount obtained was exceedingly small, only enough for the above reactions. The solution filtered from this heteroproteose was concentrated by gently boiling over a low flame.

During concentration of the solution filtered from the heteroproteose a coagulum developed as a film on the surface of the liquid and sides of the dish. We have frequently noticed that plant proteoses from various seeds coagulate in this manner although behaving in most other respects like typical proteose. This coagulum, 25, filtered out washed with water and alcohol and dried over sulphuric acid, weighed 0.29 gram and contained 16.84 per cent. of nitrogen.

The filtrate from 25 was precipitated by alcohol and gave 1.45 gram of 26, having the following composition, when dried at 110°:

MALT PROTEOSE, 26.			
	I.	II.	Average.
Carbon .....	50.61	50.64	50.63
Hydrogen .....	6.72	6.61	6.67
Nitrogen .....	16.69	....	16.69
Sulphur .....	} ....	....	26.01
Oxygen .....			
Ash .....	....	....	100.00 1.29

As will be remembered, in making these preparations, 25 and 26, the proteose was precipitated, first, by adding acetic acid to the solution containing twenty per cent. of salt and; second, by dissolving the precipitate thus produced in water and saturating the neutralized solution with salt. The filtrate, A, from the first, as well as the filtrate, B, from the second precipitation, still contained proteose.

A was therefore neutralized with sodium carbonate and saturated with salt, but, as no precipitate resulted, acetic acid was added as long as any proteid was thrown down.

B was treated similarly with acetic acid and the two precipitates thus obtained from the salt-saturated solutions were collected on the same paper and the filtrates were united and marked C. The precipitates were dissolved in water, the solution carefully neutralized, dialyzed free from chlorides and then concentrated by slow boiling. During concentration a small coagulum separated which was filtered out, washed with water and alcohol and dried over sulphuric acid. This preparation, 27, weighed 0.22 gram and contained, without correcting for ash, 16.40 per cent. of nitrogen.

An excess of alcohol was added to the filtrate from 27, and the precipitate produced, after treating in the usual manner, gave 1.49 gram of preparation 28, which, dried at 110°, had the following composition :

## MALT PROTEOSE, 28.

	I.	II.	Average.
Carbon.....	49.82	49.87	49.85
Hydrogen.....	6.69	6.64	6.67
Nitrogen.....	16.00	....	16.00
Sulphur.....	} ....	....	27.48
Oxygen .....			
			<hr/>
			100.00
Ash.....	....	....	1.54

The salt-saturated filtrate, C from which 27 and 28 had been precipitated, was neutralized and dialyzed until much of the salt had been removed, then concentrated and dialyzed until free from chloride. The solution was finally concentrated to small volume and precipitated with alcohol. The substance so

obtained, after treating as usual, weighed 6.25 grams but was found to contain 4.70 per cent. of ash and only 8.91 per cent. of nitrogen, reckoned ash-free. This precipitate, which was expected to contain *deuteroproteose*, evidently included much non-proteid matter.

It will be noticed that of the thirty-eight grams of substance taken, only a very small part was recovered. It is probable that a large share of the substance (p. 550) was non-proteid, and also that during the dialysis much proteose was lost by diffusion.

Preparation 26 has the properties of a protoproteose and may be regarded as such. Preparation 28 is a mixture of proto- and deuteroproteose. Pure deuteroproteose was not obtained, it having been impossible to separate the non-proteid substances associated with it.

It thus appears that at least two protoproteoses exist in malt, for 26 has much less carbon than the mixtures of proteose and albumin, 17 to 24. Preparation 17 contains about ninety-five per cent. of proteose and has 53.16 per cent. of carbon, whereas 26 has only 50.63 per cent. of carbon. This difference can scarcely be due to non-proteid impurities, for 26 contains even more nitrogen than 17. According to the definitions now accepted, a protoproteose is any form of proteid which is soluble in pure water, uncoagulable by heat, precipitable by saturation with sodium chloride, and gives a pink biuret reaction and a precipitate with nitric acid that dissolves on warming and reappears on cooling. The protoproteoses obtained by artificial digestion, usually have a composition varying with that of the proteids from which they are derived, and the proteoses of malt may also be expected to differ according as they originate from one or another of the several proteids of barley. While the plant proteoses resemble the digestive proteoses in the reactions just specified, some of their physical properties are so different that it is not improbable that they are quite distinct substances.

#### MALT PROTEID SOLUBLE IN DILUTE ALCOHOL. BYNIN.

Three kilograms of ground malt were extracted with alcohol of 0.90 sp. gr. The extract was filtered clear, and concentrated to about one-third its original volume, on a water bath.

When cool the solution was poured off from the separated proteid and the latter was washed with dilute salt solution, with water, with ether to remove adhering water, and finally with absolute alcohol. Dried over sulphuric acid, this preparation, 29, weighed 33.1 grams, being 1.11 per cent. of the malt.

Dried at 110° it had the following composition :

BYNIN, 29.			
	I.	II.	Average.
Carbon .....	55.01	54.93	54.97
Hydrogen.....	6.77	6.49	6.63
Nitrogen.....	15.98	16.13	16.06
Sulphur .....	0.94	....	0.94
Oxygen.....	....	....	21.40
			<hr/>
			100.00
Ash .....	....	....	0.67

In order to fraction this substance, twenty-seven grams were dissolved in alcohol of 0.70 sp. gr., the solution filtered perfectly clear, concentrated to small volume and poured into absolute alcohol, a few drops of ten per cent. salt solution being added to cause the proteid to separate. The precipitate so produced was filtered out, treated with absolute alcohol and dried over sulphuric acid. This preparation, 30, weighed twenty grams, and when dried at 110° had the following composition :

BYNIN, 30.			
	I.	II.	Average.
Carbon .....	54.74	55.08	54.91
Hydrogen .....	6.61	6.62	6.62
Nitrogen.....	16.21	16.06	16.14
Sulphur .....	0.83	....	0.83
Oxygen.....	....	....	55.07
			<hr/>
			100.00
Ash .....	....	....	0.40

Of preparation 30, sixteen grams were dissolved in 180 cc. of warm alcohol of fifty per cent. by volume, and a part of the proteid precipitated by cooling to 0° C. The solution was decanted and the precipitate, 30a, was treated as just described for 30. The substance now separated, 30b, was treated in the same manner. 30c, thus obtained, was dissolved in a little strong

alcohol and the perfectly clear solution poured into absolute alcohol, adding also a few drops of ten per cent. salt solution. The precipitate was then dehydrated with absolute alcohol and dried over sulphuric acid. This preparation, 31, weighed eight and three-tenths grams and gave the following results on analysis :

BYNIN, 31.			
	I.	II.	Average.
Carbon .....	55.07	....	55.07
Hydrogen .....	6.75	....	6.75
Nitrogen .....	16.18	16.42	16.30
Sulphur .....	0.84	....	0.84
Oxygen.....	....	....	21.04
			<hr/> 100.00
Ash.....	....	....	0.10

The solutions containing fifty per cent. of alcohol, which had been decanted from 30a, 30b and 30c were united, concentrated to small volume, cooled, and the liquid poured off from deposited substance. The latter, dehydrated with absolute alcohol and dried over sulphuric acid—preparation 32—weighed five grams.

As seen from the following table, these analyses show that the proteid has not been separated into fractions of differing composition.

SUMMARY OF ANALYSIS OF BYNIN.					
	29.	30.	31.	32.	Average.
Carbon .....	54.67	54.91	55.07	55.16	55.03
Hydrogen .....	6.63	6.62	6.75	6.67	6.67
Nitrogen .....	16.06	16.14	16.30	16.53	16.26
Sulphur .....	0.94	0.83	0.84	0.76	0.84
Oxygen .....	21.40	21.50	21.04	20.88	21.20
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00
Ash.....	0.67	0.40	0.10	0.16	

These figures are, except for hydrogen, in remarkably close agreement with those given by Chittenden and Osborne for the composition of zein, the alcohol soluble proteid of maize ; but in properties the two bodies are very distinctly different. Compared with hordein, the alcohol soluble proteid of barley, this malt proteid contains about one per cent. more carbon and one per cent. less nitrogen.

## ALCOHOL SOLUBLE PROTEIDS.

	Hordein of barley.	Bynin of barley malt.	Zein of maize.
Carbon .....	54.29	55.00	55.23
Hydrogen .....	6.80	6.67	7.26
Nitrogen .....	17.21	16.26	16.13
Sulphur .....	0.83	0.84	0.60
Oxygen .....	20.87	21.20	20.78
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

## MALT PROTEID INSOLUBLE IN WATER SOLUTION AND DILUTE ALCOHOL.

The proteid remaining undissolved, after extracting malt with water, salt solution and alcohol, was not separated or identified, but its presence in considerable quantity was shown, as follows :

After extracting 100 grams of malt first, with ten per cent. sodium chloride solution, and then with alcohol of 0.90 sp. gr., dehydrating with absolute alcohol and drying in the air, a residue was obtained which weighed seventy-five grams and contained 0.82 per cent of nitrogen, equivalent to 0.62 per cent. reckoned on the original malt. Assuming, as is probably true, that this nitrogen belongs to proteid matter, we have in the residue three and eight-tenths per cent. of proteid, insoluble in the reagents named.

## SUMMARY.

In the malt used in this investigation we have found :

1. *Bynedeitin*, readily soluble in very dilute salt solution, therefore largely passing into the aqueous extracts because of the soluble salts of the seed. This globulin contains two per cent. more carbon and three per cent. less nitrogen than edestin, the globulin of barley, and is much more soluble in very dilute salt solutions than edestin.

The composition of this globulin, as shown by the average of eleven analyses, is :

## BYNEDESTIN.

Carbon .....	53.19
Hydrogen .....	6.69
Nitrogen .....	15.68
Sulphur .....	1.25
Oxygen .....	23.19
	<hr/> 100.00

Bynedestin, dissolved in ten per cent. sodium chloride solution, gives a turbidity at 65° and a flocculent coagulum at 84°, but, even after heating for some time at 100°, the coagulation is far from complete.

This proteid is not precipitated by saturating its solutions with sodium chloride, and but partly precipitated by saturating with magnesium sulphate.

2. *Leucosin*, an albumin, identical in composition and properties with the leucosin found in wheat, rye and barley. The composition of this proteid was found to be :

MALT ALBUMIN, LEUCOSIN.	
Carbon.....	53.07
Hydrogen.....	6.72
Nitrogen.....	16.71
Sulphur.....	} 23.50
Oxygen.....	
	<hr/>
	100.00

Leucosin is intimately associated with diastase.<sup>1</sup> Heated to 59°, solutions of this proteid become turbid, and at 58° a flocculent coagulum occurs. Coagulation, however, is incomplete unless the solution is heated for some time and the temperature raised to about 70°. Saturation with sodium chloride or with magnesium sulphate partly precipitates leucosin.

3. A *Protoproteose* readily precipitated from aqueous solution by adding an equal weight of alcohol. No preparations of this body were obtained free from albumin. Its composition is nearly the same as that of leucosin, since preparations containing from ninety to fifty per cent. of it, together with from ten to fifty per cent. of leucosin, are not distinguishable by analysis.

4. A *Protoproteose* less readily precipitated by alcohol than the preceding, and of a different composition, as shown by the following figures :

MALT PROTOPROTEOSE.	
Carbon.....	50.63
Hydrogen.....	6.67
Nitrogen.....	16.69
Sulphur.....	} 26.01
Oxygen.....	
<hr/>	
100.00	

<sup>1</sup> See papers on Diastase, Annual Reports of Conn. Agr. Expt. Station, 1894. pp. 202, 204, and 1895, p. 238; also this JOURNAL, 17, 587; 18, 536.



That this is not an impure preparation of the preceding, is indicated by the fact that the amount of nitrogen is alike in both, while the carbon differs by two per cent. This difference would probably not be caused by non-proteid impurities. It is possible that the deuteroproteose next to be described, may not have been completely separated by the process employed.

5. A *Deuteroproteose* which could not be separated from non-proteid impurities.

6. A *Heteroproteose* in extremely small amount.

7. *Bynin* a proteid insoluble in water and saline solutions, but readily soluble in dilute alcohol. About 1.25 per cent. of this proteid was obtained from the malt, having the following composition :

BYNIN.	
Carbon .....	55.03
Hydrogen .....	6.67
Nitrogen .....	16.26
Sulphur.....	0.84
Oxygen .....	21.20
<hr/>	
100.00	

8. A proteid insoluble in water, in salt solution and in alcohol, amounting to 3.80 per cent. The composition and properties of this proteid we have been unable to determine.

#### PROPORTIONS OF THE VARIOUS PROTEIDS IN MALT.

Assuming twenty-one per cent. of the total nitrogen of the malt to exist in non-proteid bodies, and admitting the malt proteids to contain on the average 16.3 per cent. of nitrogen, we have, in the malt investigated, a total of 7.84 per cent of proteids.

As already indicated, p. 555, proteid equal to three and eight-tenth per cent. of the malt was insoluble in alcohol and in salt solution.

It was shown on page 553 that 1.11 per cent. of proteid was recovered from alcohol solution, and making allowance for loss, we may place the amount of alcohol-soluble proteid at 1.25 per cent.

Subtracting the sum of the insoluble proteid and the alcohol soluble proteid from the total malt proteids, we have 2.79 per

cent. for proteids soluble in salt solution, *viz.*, globulin, albumin, and proteoses.

The amount of coagulable proteids was found to be 1.50 per cent., consisting of albumin and a part of the globulin. There remains then 1.29 per cent. for the uncoagulated globulin and the various proteoses. We have accordingly, in the malt used for these determinations, approximately :

	Per cent.
Proteid, insoluble in salt solution and in alcohol.....	3.80
Bynin, soluble in dilute alcohol.....	1.25
Bynedestin, leucosin and proteoses } { Coagulable.....	1.50
soluble in water and salt solution } { Uncoagulable.....	1.29
Total proteids.....	7.84

The results of this study show : that, in germination, the proteids of barley undergo extensive changes without acquiring, or before acquiring the properties of proteoses ; that hordein disappears and an alcohol soluble proteid of entirely different composition takes its place ; that edestin also disappears and a new globulin is formed, very different both in composition and properties. The albumin, on the other hand, appears to be unchanged in its characters, but its quantity is increased. It is to be noted also that hordein and edestin are both replaced by proteids much richer in carbon and poorer in nitrogen.

#### NOTE.

*A Cheap Adjustable Electrolytic Stand.*—Stands for electrolytic work, especially for efficient assaying of copper, should fulfill certain conditions.

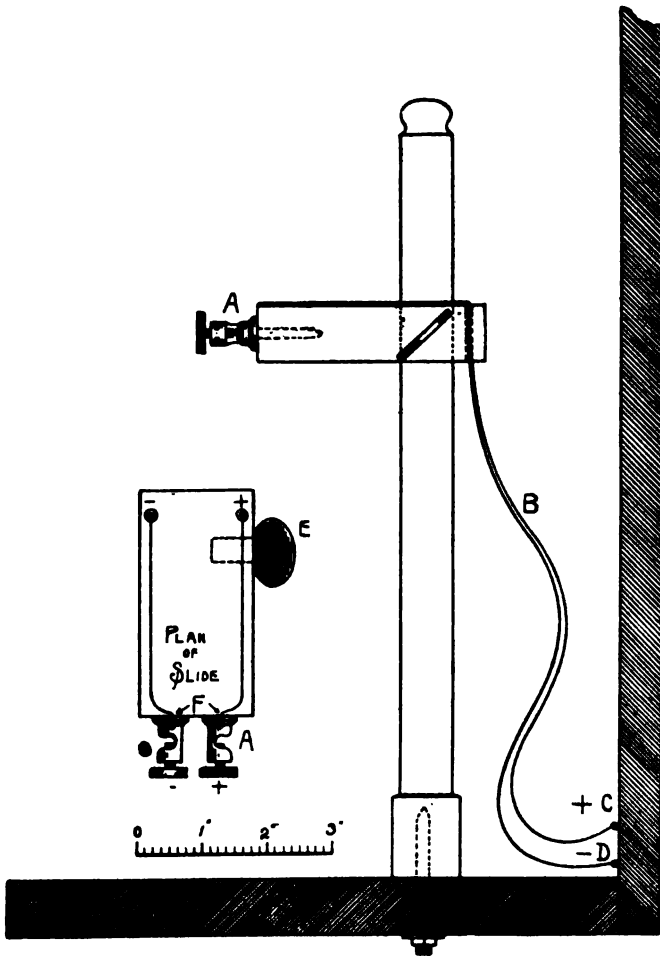
All joints and connections, as far as possible, should be permanently soldered and very few switches used.

If many assays of the same kind are to be simultaneously conducted, each assay should be independent of its neighbor.

The stands or terminals, for holding the platinum cases or cylinders and spirals (which are the forms of electrodes generally used in large laboratories), should be capable of instant adjustment to suit a beaker of any height and size, or permit a block of wood to be placed under the beaker, since some chemists

prefer when an electrolysis is finished, to wash the electrodes by quickly slipping out a block, dropping the beaker, and replacing it with another of distilled water.

The author has designed and used for several years, electro-



lytic stands which are simple in construction and comparatively inexpensive, and a number of them may be quickly turned

out together in any works possessing a carpenter or machine shop.

The drawing shows that the stands each consist of small, turned sticks of oak wood, one foot high, and fastened by a short lag screw, bolt, or common screw and washer, to a wooden shelf one inch thick, under which are placed the gravity or storage batteries.

A block of wood, of the shape and construction given in the sketch, is arranged to slide on the wooden post, and fastened by the large screw (*E*). Into the front end of the sliding block are screwed two brass holders for the "cylinders," or "cone and spiral" electrodes.

All dimensions may be taken from the scale accompanying the sketch. The "single binding posts" given in chemical catalogues, make very good holders if one side of the brass post is filed out opposite the hole as shown in cut (at *A*.)

The cotton-covered (No. 19) connecting wires (*B*) are connected by soldered joints with two parallel main wires (No. 16) at *C*, *D*, and are led up through two small holes at the back of the sliding block and over the top to the brass plugs in front.

These holders or plugs may be screwed in part way, and the bared ends of the wire twisted once around the screw.

The brass plugs are then screwed up tightly in position, the short, free end of the wire bent down over the top in a little slot previously filed, and fastened with a drop of solder (as at *F*.)

These neat, wooden stands may be set in a single or in a double row in a "staggering" position.

The stands may be arranged in little sets of twos or fours, independent of each other, by breaking one of the parallel main wires at *C* or *D* by a switch or removable plug of low resistance.

From each of these groups or sets lead wires with soldered connections may be run to batteries below, and to arrangements of incandescent lamps on the wall above and behind the row of stands, and each group of assays may thus be given a different strength of current, one sixteen candle power lamp being generally sufficient for four copper assays.

The advantage of connecting assays of the same kind in parallel, as indicated in the sketch, consists mainly in the fact

that the current is divided up between the assays, lessening the total resistance, and that any electrode may be quickly removed after loosening the screw at *A* without disturbing the other analyses.

If the laboratory is wired for incandescent (seventy-five volt) lamps, the current obtained from a circuit containing arrangements of sixteen or thirty-two candle power lamps is more steady than that from small batteries.

If the dynamo only runs at night, a bank of lamps in parallel arc may be arranged as a resistance and the current passing through these, caused to charge two or more storage batteries in series at night. In the morning the direct current, through resistance of lamps, which had been applied to analyses during the night, may then be switched off and the dynamo current also switched off from storage cells, which are then connected up, through suitable resistance coils, in an opposite direction with the copper analyses yet unfinished.

As noted, adjustable resistance coils should be included in the circuit of analyses, through which the storage cells discharge. For a description of such apparatus, I refer to the works of well known authorities,<sup>1 2</sup> and for different arrangements of incandescent lamps to articles in this Journal of 1894 and 1895.

The "chloride accumulator" is thought to be the most efficient storage cell for laboratory work. Three cells in series of the type (5 E, Electric S. Bat. Co., Phila.), require the current of ten sixteen-candle-power lamps in parallel arc to secure a full charge in one night of twelve to fourteen hours, and will, when connected with analyses, give out again for a period of fourteen to fifteen hours about eighty per cent. at two volts potential.

The foregoing descriptions will, it is hoped, be of service to those who have considerable electrolytic work with copper, or other metals, and the stand described is recommended as one that is permanent, easily adjustable and comparatively inexpensive, if set up by the chemist himself.

G. L. HEATH.

<sup>1</sup> *Clasen's Quant. Anal. by Elect.*, Am. Ed., pp. 23-28.

<sup>2</sup> *E. F. Smith's Electrolysis*, pp. 27-28.

## NEW BOOKS.

**WATER SUPPLY (CONSIDERED PRINCIPALLY FROM A SANITARY STAND-POINT).** BY WILLIAM P. MASON. 8vo. viii, 504 pp. New York: John Wiley & Sons. Price, \$5.00.

There is scarcely a subject about which chemists are called upon to give an opinion, which requires broader knowledge, more care in analytical work and, above all, more exercise of good common sense, than the determination of the sanitary character of a water supply.

The present work will be found of service not only to chemists, but also to physicians, engineers, and many others who are called upon to consider problems of this kind.

The author has had a wide practical experience in the study of water supplies and shows excellent judgment selecting that which is most valuable, both from his own experience and from the almost boundless literature of the subject.

In a long chapter on Drinking Water and Disease, a good selection is given from the many cases on record where epidemics, especially of typhoid fever and of cholera, have been proved to have been connected with the use of a contaminated water.

The chapter on the artificial purification of water gives a detailed account of the best systems in use in America and in Europe for the filtration of water on a large scale. A large number of plants of this character have been personally examined by the author.

In discussing the natural purification of water it is interesting to notice that the author agrees with those who believe that the self-purification of a river water which has once been seriously contaminated with sewage is a very slow process, and that such waters should not be recommended for potable use even after many miles of flow. The evidence given on this point seems to be almost incontrovertible.

About one-third of the book is given to the discussion of the various forms of natural waters: rain, ice, snow, river water, stored water, ground water and deep-seated water.

Concise and satisfactory directions are given for the chemical

and bacteriological examination of waters, the latter being confined to methods of preparing culture liquids and counting colonies. In the opinion of the writer the retort which is recommended for the "albuminoid" ammonia process would be better replaced by a flask, or a distilling bulb with a ground glass stopper. The retort seems to have little place left in the modern laboratory.

The opinion is expressed that, while the bacteriological examination is important, its value has been greatly overrated, and the chemical examination will, in most cases, give more reliable information as to the character of a water.

The typography and general arrangement of the book are excellent; and the writer is not acquainted with any other work which contains so much that is of value on the subject.

W. A. NOYES.

**HINTS ON THE TEACHING OF ELEMENTARY CHEMISTRY IN SCHOOLS AND SCIENCE CLASSES.** By William A. Tilden, D.Sc., F.R.S. London: Longmans, Green & Co. 1895. 12mo. 84 pp. Ill. Price, 75 cents.

Dr. Tilden is one of the English chemists who examines many papers written by candidates in chemistry. He is well qualified, therefore, to speak to teachers of the subject, and his book is practically a series of short talks to teachers. The following extract gives a good idea of his point of view:

"In order to cultivate the powers of observation, various branches of natural science have been brought into use in schools, but none seem to present so many advantages as are offered by chemistry when rightly taught. As a science based entirely upon the results of observation and experiment, it is only by making experiment a principal feature of the system of instruction that these advantages can be secured. The observations and experiments must also, as far as possible, be the work of the pupil and not of the teacher, and therefore exercises undertaken should be in the first instance of the simplest possible character, and graduated so as to lead on to more difficult operations, which should only be undertaken after some time and after demonstration by the teacher. It is a mistake to suppose that the great theories of chemistry can be established by experiments conducted wholly by beginners, but with due preliminary

instruction the more advanced student may get a long way in this direction."

Prof. Tilden seems to fully comprehend the necessity for simplicity in the apparatus to be used by beginners and a number of hints are given in this line worth consideration.

EDWARD HART.

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### BOOKS RECEIVED.

Bulletin No. 41. Experiments with Wheat and Oats. University of Illinois, Agricultural Experiment Station, Urbana, Ill. 16 pp.

Bulletin No. 42. Corn Experiments. University of Illinois, Agricultural Experiment Station, Urbana, Ill. 18 pp.

Chemistry at a Glance. A Study in Molecular Architecture. By Herbert B. Tuttle. No. 1. Oxides. 1896. 59 pp. Price, 60 cents.

A Dictionary of Chemical Solubilities. (Inorganic.) By Arthur Messenger Comey, Ph.D. London: Macmillan & Co., and New York. 1896. xx, 515 pp. Price \$5.00.

Experimental-Untersuchungen über Zersetzung und Verbrennung von Kohlenwasserstoffen. By Fritz Haber. München: R. Oldenbourg. 1896. 116 pp. Price M 1.50.

Elementary Chemistry. By Paul C. Freer. Boston: Allyn & Bacon. 1895. x, 284 pp. Introductory price, \$1.00.

Bulletin No. 41. Tobacco. Yellow Leaf and Cigar Varieties. Agricultural Experiment Station, Baton Rouge, La. 32 pp.

Nineteenth Annual Report of the Connecticut Agricultural Experiment Station for 1895. Part II. Fertilizer Experiments. New Haven: Connecticut Experiment Station. 157 pp.

The Liquefaction of Gases. Papers by Michael Faraday, F.R.S., with an appendix. Alembic Club Reprints, No. 12. Edinburgh: Wm. F. Clay. 79 pp. Price, two shillings.

Nineteenth Annual Report of the Connecticut Agricultural Experiment Station for 1895. Part III. Proteids of Potato; of Pea and Vetch; Conglutin and Vitellin. Recent Laws affecting the Station: Index. New Haven, Conn.: Connecticut Agricultural Experiment Station. 88 pp.



# THE JOURNAL

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## AMERICAN CHEMICAL SOCIETY.

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### THE VALUE OF LEATHER REFUSE.

BY J. B. LINDSEY.

Received May 14, 1896.

#### I. RAW, ROASTED OR STEAMED LEATHER.

IN another publication<sup>1</sup> the writer reviewed the experiments made by various investigators concerning the agricultural value of different forms of leather refuse, and drew the following conclusions: "The results of both field and pot experiments, as well as artificial digestion experiments, indicate that leather, either raw, roasted or steamed, is a very inferior source of plant food. Carefully conducted experiments by Wagner give the nitrogen it contains a relative value of 20, the nitrogen in sodium nitrate being valued at 100. When nitrogen in organic matter is valued at from sixteen to eighteen cents per pound, nitrogen in raw, roasted or steamed leather should be worth but from three to six cents per pound.

#### II. DISSOLVED LEATHER.

Deherain and others have suggested that if leather be dissolved in sulphuric acid, its nitrogen will be made as available as that contained in the average animal matter. It is generally understood that many European manufacturers of fertilizers thus turn leather waste to account. No direct experiments are on record, so far as the writer is aware, to bear out the above claim.<sup>2</sup>

In order to study the value of dissolved leather, pot experi-

<sup>1</sup> Twelfth annual report of the Massachusetts Experiment Station, 1894. See also *Agricultural Science*, 8, Nos. 2 and 3.

<sup>2</sup> See however a single test reported in the Report of Connecticut Experiment Station for 1894, p. 101.

ments with oats were conducted during the years 1894 and 1895. The results obtained in 1894 have already been published.<sup>1</sup> The results for both years are presented below :

*General Plan of the Experiment.*—The experiments were conducted in galvanized iron pots. The soil, poor in all three ingredients of fertility, was supplied with an excess of potash and phosphoric acid. The nitrogen in sodium nitrate was taken as a standard, being rated at 100. The same quantity of nitrogen in sodium nitrate, Philadelphia tankage (roasted leather) and dissolved leather was applied to different sets of two or three pots each ; one set of pots received no nitrogen. These latter pots measured the nitrogen capacity of the soil. The entire number of pots were treated as nearly alike as possible so far as sunlight, moisture, etc., were concerned. With similar conditions and plant food alike, excepting the nitrogen source, it is clear that the amount of nitrogen taken up by the plants in the different pots, would be a measure of the availability of the nitrogen in the several forms of nitrogen-containing material.

*The Pots Used.*—The pots, of thin galvanized iron, were seven and three-fourths inches in diameter and eight inches deep. A galvanized iron tube, half an inch in diameter, extended from the top to the bottom of the pot, connecting at the base with a second tube of the same material one inch in diameter. The latter tube extended along the bottom of the pot, and was perforated with small holes. The object of these tubes was to supply water partly from the bottom of the pot.

#### EXPERIMENTS A.

These experiments were begun in 1894 with eighteen pots, three parallel pots for each distinct test ; they were continued in 1895 with twelve pots, two pots being employed for each test.

*The Soil.*—The soil was of a gravelly nature, and had not been cultivated for a long time. It was very poor in all three ingredients, as the following analysis will show :

	Per cent.
Water when tested.....	14.25
Phosphoric acid.....	0.13
Potassium oxide.....	0.08
Nitrogen .....	0.09

<sup>1</sup> *Loc. cit.*

**Fertilizers Used.**—The sources of nitrogen were sodium nitrate, Philadelphia tankage,<sup>1</sup> and dissolved leather. The dissolved leather was prepared in 1894 by heating 210 grams of C. P. sulphuric acid of 50° B. to 80° C. and slowly adding sixty-three grams of finely ground sole leather. The mixture was thoroughly stirred and allowed to stand one-half hour. A dark pasty mass resulted, to which were added forty-nine grams of water to thin somewhat, together with sufficient calcium carbonate to neutralize the excess of sulphuric acid, and to make the resulting mass suitable to handle. The calcium carbonate was used in preference to the phosphate, in our case, to avoid an excess of phosphoric acid. After standing twenty-four hours the mixture became dry and friable. The dissolved leather for 1895, was prepared in the same way, excepting that the water was omitted. Double superphosphate was used as a source of phosphoric acid, and potash was applied in the form of the double sulphate of magnesia and potash.

## COMPOSITION OF FERTILIZERS USED.

	Nitrogen. Per cent.	Available phosphoric acid. Per cent.	Total phosphoric acid. Per cent.	Potas- sium oxide. Per cent.
Sodium nitrate for 1894 and 1895..	14.28	....	....	....
Dissolved leather, I., 1894 .....	0.97	....	....	....
" " I., 1895 .....	0.97	....	....	....
Philadelphia tankage 1894 and 1895	7.80	....	....	....
Double superphosphate 1894 and 1895.....	..	47.42	47.80	
Double sulphate of magnesia and potash, 1894.....	....	....	....	24.32
Double sulphate of magnesia and potash, 1895.....	....	....	....	25.08

## ARRANGEMENT OF THE EXPERIMENT.

1894.			
Source of nitrogen.	Amount of nitrogen ap- plied per pot. Gram.	Amount of available phos- phoric acid ap- plied per pot. Grams.	Amount of potassium oxide applied per pot. Grams.
Pots 1, 2, 3, soil nitrogen....	0.00	1.20	2.40
" 7, 8, 9, sodium nitrate..	0.30	1.20	2.40
" 13, 14, 15, dissolved leather	0.30	1.20	2.40
" 10, 11, 12, sodium nitrate..	0.60	1.20	2.40
" 16, 17, 18, dissolved leather	0.60	1.20	2.40
" 4, 5, 6, Phil. tankage ...	0.60	1.20	2.40

<sup>1</sup> Roasted leather.

Pots 1, 4, 7, 10, 13, 16, were infected with a small quantity of cultivated soil, to note if the infection facilitated to any marked degree the nitrification of the organic nitrogen in case of these particular experiments. To each of these pots was also added ten grams of air-slaked lime.

1895.			
Source of nitrogen.		Amount of nitrogen ap- plied per pot. Grams.	Amount of available phos- phoric acid per pot. Grams.
			Amount of potassium ox- ide per pot. Grams.
Pots	1, 2, soil nitrogen.....	0.00	2.40
"	7, 8, sodium nitrate .....	0.30	2.40
"	13, 14, dissolved leather ...	0.30	2.40
"	10, 11, sodium nitrate .....	0.60	2.40
"	16, 17, dissolved leather ...	0.60	2.40
"	4, 5, Phil. tankage.....	0.60	2.40
			4.80
			4.80
			4.80
			4.80
			4.80
			4.80

It will be noticed that double the quantity of phosphoric acid and potash was applied in 1895, to make sure of a sufficient amount to enable the nitrogen to do its best work. To each of the pots was added ten grams of air-slaked lime. The same soil was used in 1895 as in 1894.

*Filling the Pots.*—About an inch of good clean gravel was first placed in the pots. All of the fertilizer excepting the nitrate was then mixed with eleven and one-half pounds of soil, which was put in in layers and gently pressed down. One-half gram of selected oats was then scattered over the soil, and covered with one pound of earth. The pots were thus filled to within one centimeter of the rim. One-half of the nitrate was applied in solution at the time of seeding, and the other half five to six weeks later.

*General Care of the Pots.*—The pots were set into a wagon running on an iron track. The floor of the wagon was surrounded with sides six inches deep. The pots were carefully watched and kept sufficiently watered. A portion of this water was supplied from beneath, and the remainder was added to the surface by the aid of a sprinkling pot. Sometimes it was necessary to water twice daily. The pots were kept in the open whenever the weather permitted. During wet or windy weather, and at night, they were run under cover.

*Harvesting, etc.*—The plants in pots 1, 2, 3, 4, 5, 6, in 1894, and in 1, 2, 4, 5, in 1895, were very light green and spindling during the entire growing period. The plants in the different pots were harvested as they matured. They were cut close to the soil, put in paper bags and hung away to dry. After the product of each pot was thoroughly air-dry, the grain was carefully removed, weighed, coarsely ground, and dry matter determinations made. The straw was cut into short lengths, and also tested for dry matter. Finally both grain and straw were ground fine, and nitrogen determinations made.

The figures in Tables I and II show the results obtained in two years. The first column in Table I shows the amount of nitrogen applied to each pot. The next four columns show the average dry matter produced for both years. The four columns next following indicate the gain in dry matter over soil nitrogen pots. The last column shows the average gain in dry matter of straw and grain for two years, produced by the different fertilizers, the gain produced by sodium nitrate being reckoned at 100.

It will be seen that the Philadelphia tankage has been but slightly available as a nitrogen source. Its effect the second year was rather better than during the first season. The combined results for the two years show it to be very inferior to the sodium nitrate, yielding practically one-tenth as much dry matter. These results simply confirm the investigations made by others with different forms of untreated leather.

The results with dissolved leather are very different. One could easily observe that during the entire growing season the plants treated with this substance were uniformly green, healthy, and grew continuously, being but little if any inferior in color to the sodium nitrate pots. The amount of dry matter obtained for two years with the aid of this source of nitrogen when compared with sodium nitrate, has been as 78 to 100.

The three-tenths gram of nitrogen from sodium nitrate the second year produced a poor yield of grain. This can only be accounted for from the fact that the second half of the nitrate was not applied until shortly before the grain began to head,

TABLE I.

	Nitrogen applied to each pot yearly.	Average dry matter produced.						Gain in dry matter over soil nitrogen pots, on basis of 0.3 gram of nitrogen applied.						If gain in dry matter with sodium nitrate = 100, then other sources of nitrogen would be equal to:						Average gain in straw and grain 1894 and 1895.	
		Straw.		Grain.		Straw.		Grain.		Straw.		Grain.		Straw.		Grain.		Straw.	Grain.		
		1894.	1895.	1894.	1895.	1894.	1895.	1894.	1895.	1894.	1895.	1894.	1895.	1894.	1895.						
Soil nitrogen.....	0.000	7.82	8.64	1.69	1.32	....	....	....	....	....	....	....	....	....	....	....	....	....	....		
Philadelphia tankage	0.600	8.88	11.10	1.66	2.66	0.53	1.23	±	0.67	5.40	13.75	±	31.45	100.00	100.00	100.00	100.00	100.00	7.5		
Sodium nitrate.....	0.300	17.59	17.59	6.37	3.45	9.77	8.95	4.68	2.13	100.00	68.7	100.00	68.7	100.00	68.7	100.00	68.7	100.00	78.1		
Dissolved leather....	0.300	14.35	14.79	4.25	6.00	6.53	6.15	2.56	4.69	66.8	54.7	66.8	54.7	66.8	54.7	66.8	54.7	66.8	78.1		
Sodium nitrate.....	0.600	19.54	17.28	1.85	2.50	5.86	4.32	0.08	1.19	....	....	....	....	....	....	....	....	....	....		
Dissolved leather....	0.600	19.76	19.76	4.92	5.15	5.97	5.56	1.61	1.91	....	....	....	....	....	....	....	....	....	....		

TABLE II.

	Quantity nitrogen to each pot.	Nitrogen in total dry matter produced.			Average nitrogen in 100 grams dry matter.		For every 100 parts of nitrogen applied there has been returned in straw and grain:		When sodium nitrate = 100 other sources of nitrogen equal to:		Every gram of nitrogen applied has produced in dry matter.			For every 100 parts of straw, there has been produced in grain:
		Grams.		1894 and 1895.	Straw. Grams.	Grain. Grams.	1894.	1895.	1894 and 1895.	Straw. Grams.	Grain. Grams.	Straw and Grain. Grams.		
		1894	1895											
Soil nitrogen.....	0.000	0.094	0.105	0.100	0.76	2.50	....	....	....	....	....	....	18.2	
Phila. tankage.....	0.600	0.126	0.163	0.144	0.94	2.39	5.3	9.67	11.00	11.00	1.12	3.61	38.1	
Sodium nitrate.....	0.300	0.305	0.305	0.305	0.97	2.84	70.0	66.70	100.00	100.00	11.34	42.54	36.3	
Dissolved leather....	0.300	0.210	0.273	0.241	0.71	2.70	39.0	56.00	70.00	70.00	12.07	33.20	57.2	
Sodium nitrate.....	0.600	0.425	0.436	0.430	1.98	3.04	55.0	55.17	80.00	80.00	....	....	12.5	
Dissolved leather....	0.600	0.325	0.374	0.349	1.00	2.99	39.0	44.83	62.00	62.00	....	....	31.7	

and that this was not early enough for the plant to work it over into organic combination.

In cases where six-tenths of a gram of nitrogen was applied in the form of sodium nitrate but little grain was produced. This might be the result of two causes. First, because an excess of soluble nitrogen interfered with its natural transformation into organic combination, and in the next place it is possible, as already stated, that the second application was made too late. It is believed that the amount of phosphoric acid and potash applied especially the second year was in all cases sufficient. The six-tenths gram of nitrogen from the dissolved leather did rather better work than that from sodium nitrate, but it was still much inferior to that performed by three-tenths gram.

The amount of nitrogen obtained by the plant is a better measure of the availability of the nitrogen than the dry matter produced. This will be found in Table II. The first portion of the table shows the nitrogen in the total dry matter produced, and the average per cent. of nitrogen in 100 grams of dry matter. Next to be noted is the amount of nitrogen returned in the straw and grain, for every 100 parts of nitrogen applied. The results obtained from the several sources of nitrogen are then compared with the nitrogen obtained by the straw and grain of the sodium nitrate pots reckoned at 100. This comparison shows that the plants were able to take only about one-tenth as much nitrogen from Philadelphia tankage as from sodium nitrate, while they secured seven-tenths as much nitrogen from the dissolved leather as from the nitrate. When six-tenths gram of nitrogen was applied in the form of sodium nitrate and in dissolved leather, both the straw and grain contain a higher percentage of nitrogen than when but three-tenths gram was applied; the yield of straw and especially of grain was proportionately less, however, when the larger quantity was added. It is evident that a portion at least of the nitrogen taken up had not been turned to account in the production of organic substance.

#### EXPERIMENT B.

In this experiment, made in 1895, a soil was selected even poorer in nitrogen than the one used in Experiment A. The

object of this experiment was to see if more leather—than the amount used in the previous experiment—could not be added to the same quantity of stronger sulphuric acid, and thus secure a fertilizer testing higher in nitrogen. Dissolved leather II was therefore prepared by adding sixty grams of fine ground sole leather to 120 grams of 60° B. sulphuric acid heated to 200° F. The black pasty mass was allowed to stand for one-half hour, and was then dried off with calcium carbonate.

Dissolved leather III was prepared by adding 100 grams fine sole leather to 120 grams of 60° B. sulphuric acid. This amount of leather and acid—nearly one to one—furnished a very thick paste. It was dried off with calcium carbonate. The two dissolved leathers contained the following percentages of nitrogen:

	Per cent.
Dissolved leather II .....	1.13
“ “ III .....	1.75

The composition of the sulphate of potash and magnesia and of the double superphosphate, as well as the quantity applied, was the same as in Experiment A for 1895. The method of filling the pots, planting, and harvesting, was also similar.

Tables III and IV express the results in a similar way as Tables I and II. The sodium nitrate pots produced rather less grain than those to which the dissolved leather was applied. This tendency was noted in Experiment A. The three-tenths gram of nitrogen in the form of dissolved leather II produced about nine-tenths as much dry matter as did a like quantity of nitrogen in the form of sodium nitrate. The percentage of nitrogen in the dissolved leather plants is noticeably less however. The six-tenths gram of nitrogen from both the sodium nitrate and dissolved leather did not produce proportionately as much dry matter as did three-tenths gram, thus indicating that the plant was not able to work it all over into organic matter.

The three-tenths gram of nitrogen from dissolved leather III produced rather more dry matter than did the same quantity of nitrogen from sodium nitrate. The percentage of nitrogen in the straw and grain was decidedly less however.

Table IV shows that the oat plants were able to get but sixty-five per cent. as much nitrogen from dissolved leather II and III



TABLE III.

	Quantity of nitrogen to each pot. Grams.	Dry matter yielded by single pots.		Average dry matter from two pots.		Gain in dry mat- ter over soil nitro- gen pots on basis of 0.3 grams nitro- gen applied.		If gain in dry mat- ter with sodium nitrate=100, then other sources of nitrogen equal to:		Average Straw and Grain. Grams.
		Straw. Grams.	Grain. Grams.	Straw. Grams.	Grain. Grams.	Straw. Grams.	Grain. Grams.	Straw. Grams.	Grain. Grams.	
Soil nitrogen .....	0.000	3.146	0.296	3.706	0.426	....	....	....	....	....
Sodium nitrate .....	0.000	4.266	0.557	12.695	3.807	8.989	3.381	100.00	100.00	100.00
Disolved leather II...	0.300	12.104	3.057	11.122	4.117	7.416	3.691	82.5	109.00	89.8
Sodium nitrate .....	0.300	13.286	4.557	16.836	3.742	6.565	1.658	73.00	49.00	60.5
Disolved leather II...	0.600	15.628	3.014	17.344	6.612	6.819	3.093	75.9	91.5	80.1
Disolved leather III..	0.600	18.044	4.470	12.976	4.879	8.958	4.454	99.6	131.8	108.4
Disolved leather III..	0.300	18.582	6.578	12.352	4.882					

TABLE IV.

	Quantity of nitrogen to each pot.	Nitrogen yielded in total dry matter.	Nitrogen in 100 grams of dry matter.		For every 100 parts of nitrogen applied, there has been returned in straw as grain :	When sodium nitrate=100 other sources of nitrogen equal to :	For every gram of nitrogen applied there has been produced in dry matter :			For every 100 parts straw there has been produced in grain :
			Straw. Grams.	Grain. Grams.			Straw. Grams.	Grain. Grams.	Straw and Grain. Grams.	
Soil nitrogen .....	0.000	0.041	0.82	2.52	.....	.....	.....	.....	.....	11.5
Sodium nitrate .....	0.300	0.235	0.96	2.98	65.00	100.00	29.96	11.27	41.23	37.6
Dissolved leather II .....	0.300	0.165	0.66	2.06	41.00	63.1	24.72	13.30	38.02	49.8
Sodium nitrate .....	0.600	0.412	1.78	3.01	62.00	95.4	21.90	5.53	27.43	25.3
Dissolved leather II ..	0.600	0.305	0.83	2.43	42.00	65.0	22.73	10.31	33.04	45.4
Dissolved leather III ..	0.300	0.170	0.60	1.92	43.00	66.0	29.66	14.85	44.71	49.7

as from sodium nitrate. This confirms the results obtained in Experiment A for 1894. The oat plants secured twice as much nitrogen from the six-tenths gram as from the three-tenth gram in case of the sodium nitrate and both dissolved leathers, showing that the nitrogen was fully utilized.

#### GENERAL CONCLUSIONS.

The above experiments, part of which cover two years, make clear that dissolved leather, when properly prepared, yields as available a source of nitrogen as the average animal matter used for fertilizing purposes.

The quantity of nitrogen obtained by the plants from sodium nitrate being represented as equal to 100, the quantity obtained from dissolved leather during two years has been shown to be equal to 70.<sup>1</sup>

In this connection I beg leave to add the results of the availability of the various sources of nitrogen as determined by P. Wagner. Sodium nitrate is taken as 100 in value, and the value of other sources are compared with it.

Sodium nitrate.....	100
Ammonium sulphate.....	90
Dried blood, ground horn, and green plants .....	70
Ground bone, ground fish, and flesh .....	60
Stable manure .....	45
Ground wool.....	30
Ground leather .....	20

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### THE PROTEIDS OF THE POTATO.<sup>2</sup>

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received May 21, 1896.

SO far as we can ascertain, the only investigations of the proteids obtained from the tubers of the potato have been made by Rüling,<sup>3</sup> Ritthausen,<sup>4</sup> Zöller,<sup>5</sup> and Vines.<sup>6</sup>

<sup>1</sup> The Connecticut Experiment Station, in its recently issued report for 1895, confirmed these results.

<sup>2</sup> From the report of the Connecticut Agricultural Experiment Station for 1895. Communicated by the authors.

<sup>3</sup> *Ann. Chem. (Liebig)*, 58, 306.

<sup>4</sup> *Pflüger's Archiv*, 21, 101.

<sup>5</sup> *Ber. d. chem. Ges.*, 13, 1064.

<sup>6</sup> *Journal of Physiology*, 3, 93.

Rüling contributes a partial analysis of the coagulum obtained by boiling the juice of the potato.

Ritthausen states that nearly the whole of the proteid of the potato is contained in the juice. He obtained two preparations from the juice by heating to  $65^{\circ}$  C., filtering off the coagulum and heating the filtrate to  $76^{\circ}$ . The two coagula were analyzed with results as stated beyond. He says, "these results do not contradict the assumption that the potato contains albumin, yet the content in sulphur is only one-half as great as in albumin of serum, egg and muscle.

Zöller extracted the pressed and washed potato pulp with ten per cent. sodium chloride brine and obtained a globulin, precipitable by saturating its solution with sodium chloride and when dissolved in ten per cent. sodium chloride brine coagulating on heating to  $59^{\circ}$  or  $60^{\circ}$ . From his result he concludes that the potato contains a globulin resembling myosin.

On investigating the juice of the potato Zöller obtained results which led him to conclude that the proteids therein dissolved are also globulins, but that further study was needed to explain their "peculiar deportment," especially, it is to be inferred, the fact of coagulation occurring at from  $43^{\circ}$  to  $48^{\circ}$ , and again, at  $62^{\circ}$ .

Vines states that prolonged treatment of the "crystalloids" of the potato with ten per cent. sodium chloride solution produces no apparent effect, but that they dissolve readily in a saturated solution of this salt, thus differing from all other protein crystals which he had observed.

Having had occasion to prepare a quantity of pure starch from the potato, we took advantage of the opportunity to examine the associated proteids.

After removing the skins, the tubers were crushed and squeezed in a drug press. The juice was strained through cloth and allowed to stand and deposit the greater part of the suspended matters. It was then saturated with ammonium sulphate and the precipitate so produced was filtered out. The potato pulp was washed with water and the washings after clearing were also saturated with ammonium sulphate. The

two precipitates thus obtained were united, dissolved in salt solution, filtered clear and dialyzed.

The washed pulp was then treated with ten per cent. sodium chloride solution; the proteid, thus extracted, was precipitated with ammonium sulphate, dissolved in salt solution, filtered clear, and also dialyzed. The globulin precipitated very slowly on dialysis, and after fourteen days was filtered out. The proteid obtained from the juice was much greater in amount than that from the salt extract of the pulp. The globulin, from both juice and salt extract, was then dissolved in salt solution, the solutions were united, filtered from a considerable quantity of insoluble globulin (rendered insoluble by long contact with water), and the solution again dialyzed. After freeing from chlorides, the contents of the dialyzer were filtered, the reprecipitated globulin was washed with water and alcohol and dried over sulphuric acid, giving preparation 1, weighing 7.34 grams.

The filtrate, from preparation 1, still contained proteid and was therefore saturated with sodium chloride, which completely precipitated the remaining globulin. This was then dissolved in dilute salt solution and dialyzed in water until free from chlorides and, as the proteid was not thus precipitated, the dialyzer was transferred to alcohol, which soon threw down all the proteid. This was filtered out, washed in water and absolute alcohol and dried, giving one-half gram of preparation 2.

The solutions, filtered from the globulin precipitated by the dialysis first described, were united and, in order to obtain the proteid in a solution of smaller volume, the liquid was saturated with ammonium sulphate, the precipitate produced was dissolved in a little water and the clear solution dialyzed, first in river water and then in distilled water. The globulin so precipitated was filtered out, washed with water and absolute alcohol and dried, yielding preparation 3, weighing 3.40 grams. The filtrate from this preparation was dialyzed into alcohol and the resulting precipitate filtered out, washed with absolute alcohol, and dried, forming preparation 4, which weighed 1.74 grams.

The filtrate from 4 was further dialyzed in alcohol and the proteid completely precipitated by adding absolute alcohol. This substance, after filtering out, washing with absolute alco-

hol and drying, weighed 0.53 gram and formed preparation 5.

These several preparations were analyzed after drying them at  $110^{\circ}$ , with the following results:

	POTATO GLOBULIN. TUBERIN.					Ritthausen.	
	Osborne and Campbell.					I.	II.
	1.	2.	3.	4.	5.		
Carbon....	53.62	....	53.58	53.64	....	....	53.87
Hydrogen..	6.80	....	6.91	6.83	....	....	7.30
Nitrogen..	16.15	16.29	16.36	16.34	16.07	15.76	15.98
Sulphur ..	1.22	....	1.27	23.19	....	....	0.86
Oxygen ...	22.21	....	21.88		....	....	21.99
	100.00		100.00	100.00			100.00

The close agreement in composition among our five fractions is in itself, strong evidence that, besides this globulin, but little proteid is present in the potato. These five fractions practically include the whole of the proteid matter dissolved in the juice and salt extracts. The above figures given by Ritthausen for the composition of the proteid, obtained by coagulation of the juice at  $65^{\circ}$  and  $76^{\circ}$ , are also in close agreement with ours, excepting those for sulphur. The slightly lower nitrogen content of the coagulated globulin is to be expected, since proteids generally, if not always, yield some ammonia when coagulated by heat.

The potato globulin, when heated slowly in a double water-bath, shows a wide range of variation in its coagulation point depending on the conditions under which it is dissolved.

A solution of this globulin prepared by treating a portion of preparation 1 with ten per cent. sodium chloride solution and filtering out the insoluble matter, became turbid at  $56^{\circ}$  and a flocculent coagulum separated at  $64^{\circ}$ . After heating some time at  $70^{\circ}$  the coagulum was filtered out and the filtrate, when again tested, gave a turbidity at  $72^{\circ}$  and a flocculent coagulum at  $76^{\circ}$ .

Another preparation of this globulin was extracted, in the same way, with ten per cent. salt solution, and the dissolved proteid was filtered from the insoluble matter and precipitated by saturating the solution with sodium chloride. The precipitated globulin was washed with saturated salt solution and removed from the paper mixed with a considerable quantity of the concentrated brine. Distilled water was gradually added

until all of the proteid dissolved. The resulting solution was therefore almost completely saturated with the proteid. This solution, when slowly heated in the double water-bath to  $44^{\circ}\text{C}.$ , and held at this temperature some minutes, became turbid and after a time flocculent, although the temperature remained perfectly constant. After raising the temperature to  $50^{\circ}$  it was filtered from the small coagulum which had formed and again heated, turbidity occurring at  $50\frac{1}{4}^{\circ}$  and flocks separating at  $51^{\circ}$ . After heating some time at  $56^{\circ}$  the solution was filtered from the second small coagulum and again tested. Turbidity occurred at  $58^{\circ}$  and flocks separated at  $59^{\circ}$ , gradually increasing to a large coagulum at  $66^{\circ}$ , which was filtered out. The filtrate now became turbid at  $63^{\circ}$ , flocks forming at  $66^{\circ}$ , and increasing to a considerable coagulum at  $70^{\circ}$ . The temperature was raised to  $80^{\circ}$  and the coagulum, which was about the same in amount as that formed at  $66^{\circ}$ , was filtered out. The filtrate gave only a trace of coagulum on boiling. The two coagula first formed were very small compared with the last two.

This test was then repeated with the same solution diluted with an equal volume of water. This solution was heated for some time at  $44^{\circ}$ , but remained perfectly clear. The temperature was then very slowly increased and at  $53^{\circ}$  a turbidity formed which, however, was scarcely greater at  $56^{\circ}$ . Above this temperature the turbidity increased until flocks separated at  $62^{\circ}$ , and a large coagulum formed at  $65^{\circ}$ . The solution filtered at  $66^{\circ}$ , gave a turbidity at  $66^{\circ}$ , with flocks at  $68^{\circ}$ , which formed a large coagulum on gradually raising the temperature to  $80^{\circ}$ , the filtrate from which gave no more coagulum on boiling.

The test was again repeated by mixing four parts of the same solution with one of water, and the same results obtained as with the solution diluted with an equal volume of water. This shows that within wide limits the temperature of coagulation does not depend on the relative quantity of dissolved proteid, but that the very low coagulation point of the undiluted solution was probably due to the presence of nearly enough sodium chloride to cause precipitation of the globulin. It will be noticed that coagulation of the proteid, which began at  $56^{\circ}$ , was not completed until the temperature had reached at about  $80^{\circ}$ .

This does not necessarily show the presence of several proteids, for such gradual coagulation is characteristic of most plant globulins, many being only very slowly coagulated, even by long boiling.<sup>1</sup> The coagulum separated by heating solutions of this globulin to 75° C. is very soluble, on gently warming, in extremely dilute hydrochloric acid, even acid of 0.01 per cent. dissolving the substance readily at 40°–50° C. The coagulum dissolves quickly and completely in one-tenth per cent. caustic potash solution at 20° and in one per cent. sodium carbonate solution at 70° C. These solutions are precipitated by neutralization, but the substance thrown down is not soluble in salt solutions. The low heat-coagulation point obtained for the solution of the globulin precipitated with salt and dissolved in a minimum quantity of water is in accord with that given by Zöller for the proteid similarly obtained by him from the juice of the potato, and our observations explain to some extent the questions which he considered to require further investigation.

In order to determine more definitely whether other proteids were present with the globulin, a larger quantity of filtered potato juice, obtained from potatoes which had been washed carefully, but from which the skins had not been removed, was saturated with ammonium sulphate, the precipitate was dissolved in dilute salt solution, which was then filtered and saturated with sodium chloride. The globulin thus precipitated was filtered out, the filtrate was dialyzed for twenty-four hours in order to remove a considerable part of the salt, and was then saturated with ammonium sulphate. The small quantity of proteid thus precipitated was filtered out, dissolved in a little dilute salt solution and sodium chloride added to complete saturation. A considerable part of the dissolved proteid was thereby precipitated, which was filtered out and dissolved in dilute salt solution. The resulting liquid became turbid on heating to 58° C. and flocculent at 60°. The substance was evidently a part of the globulin which had escaped precipitation on the first saturation with salt, probably owing to the presence of some constituent of the juice.

The solution filtered from the salt saturation precipitate *last*

<sup>1</sup> Chittenden and Mendel, *Journal of Physiology*, 17, 52.



described, was diluted with two volumes of water and then saturated with ammonium sulphate. The proteid thus separated was filtered out, dissolved in water, and found to yield a turbidity at  $52^{\circ}$  and a flocculent coagulum at  $58^{\circ}$ , a coagulation point not essentially differing from that of the globulin.

The whole solution was then heated for some time at  $70^{\circ}$  C. in a water-bath, the coagulum which separated was filtered out, and the filtrate, after removing a small quantity of coagulum, which separated on heating to  $75^{\circ}$ , was boiled and found to remain clear. This solution was then saturated with ammonium sulphate and the very small precipitate produced was filtered out, dissolved in a small amount of water and tested with the following results: nitric acid added to the solution in the cold gave no precipitate; saturation with sodium chloride gave no precipitate even when acetic acid was added. The biuret test was without result owing to the strong brown color of the solution. This substance therefore failed to give the most characteristic reactions of the proteoses, yet it must be considered as a proteose since in its essential properties it agrees more closely with this class of proteids than with any other.

The experiments made by Zöller on the juice of the potato were repeated by us with the same results as described by him, except that we found the solution of the precipitate produced by saturation with salt, to yield a flocculent coagulum at  $52^{\circ}$ , while Zöller's solution coagulated at  $46^{\circ}$ – $48^{\circ}$ . It has already been shown that a solution of the globulin similarly prepared gave a coagulum at  $44^{\circ}$ , and on dilution with one volume, as well as with one-fourth volume of water, the same solution coagulated at  $62^{\circ}$ . It is thus evident that the temperature of coagulation is not to be depended upon as a means of identifying this proteid with certainty. The other reactions described by Zöller are those given by the potato globulin. From these results then it would appear that by saturating the juice of the potato with sodium chloride the greater part of the globulin is precipitated, but that a not inconsiderable part remains in solution. If this is separated by saturation with ammonium sulphate and the precipitate so produced is dissolved in water, a large part of this globulin can be precipitated by again saturating with salt. The

proteid still remaining in solution is nearly all coagulable and the solution on heating behaves exactly like a solution of the globulin.

#### CONCLUSION.

The proteids of the potato tuber consist of a globulin, for which we propose the name *Tuberin*, and a proteose, the latter occurring in very small amount. The properties of tuberin were found to be as follows :

It is precipitated by saturating its solutions with sodium chloride, sodium sulphate, magnesium sulphate, or ammonium sulphate. By acetic acid or nitric acid a precipitate is given readily soluble in an excess of acid even in the presence of salts. Potassium ferrocyanide gives no precipitate until acetic acid is added. Mercuric chloride gives no precipitate, but picric acid or tannic acid throw down the globulin. With the biuret, Milon's and the xanthoproteic tests the usual reactions are given.

Tuberin is soluble in very dilute saline solutions and therefore the juice of the potato contains the greater part of this proteid. By dialysis it is precipitated slowly and incompletely because of the difficulty of removing *all* soluble salts by this process. Like other easily soluble globulins it readily changes to the insoluble modifications, so that preparations made by dialysis are to a great extent insoluble in saline solutions. In contact with alcohol it very quickly loses its solubility.

When dissolved in ten per cent. sodium chloride solution tuberin shows a somewhat variable heat-coagulation point depending on the conditions under which it is tested. In general a flocculent coagulum is formed on heating to 60°-65° C. Coagulation is, however, not complete until the solutions have been heated for some time at 80° C. The composition of this globulin was found from an average of several accordant analyses to be :

#### TUBERIN.

Carbon .....	53.61
Hydrogen .....	6.85
Nitrogen .....	16.24
Sulphur .....	1.25
Oxygen .....	22.05
	<hr/>
	100.00

## LEGUMIN AND OTHER PROTEIDS OF THE PEA AND THE VETCH.<sup>1</sup>

By THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received May 21, 1896.

### LEGUMIN.

UNDER the name Legumin, many preparations, obtained from various seeds, have been described, but in such different and often conflicting terms as to leave us completely in doubt with regard to the nature of this substance.

This confusion appears to have arisen largely through the mistaken idea, which formerly was very generally held, that all the proteids extracted from seeds by water and precipitated by acids are one and the same substance.

The methods of analysis employed by the earlier chemists were too crude or uncertain to set forth the slight differences in composition of the various plant proteids, and the difficulty of making pure preparations tended, as the subject was further studied, to add to the confusion. Since the methods of analysis have been perfected and the more recently developed modes of studying proteids introduced, legumin has received little or no attention. In recent literature legumin is most commonly referred to as a substance extracted from seeds by caustic alkalis, and more or less altered by the action of the solvent, but nothing has been done, to our knowledge, to show the nature of the original proteid.

The object of our investigation has been to examine the seeds in which legumin is said to exist and to determine as definitely as possible the composition and character of this substance.

In 1806 Einhof<sup>2</sup> recognized a proteid in beans and lentils which he considered to be different from the bodies of this class previously known.

Braconnot<sup>3</sup> named this substance legumin.

Noad<sup>4</sup> prepared and analyzed legumin from peas and beans.

Norton<sup>5</sup> prepared legumin from peas, sweet almonds, and oats, and gave analysis of his preparations.

<sup>1</sup> From the Report of the Connecticut Agricultural Experiment Station for 1895. Communicated by the authors.

<sup>2</sup> Gehlens: *J. d. Chem.*, 6, 543.

<sup>3</sup> *Ann. de Chim. et de Phys.*, 34, [2] 68, 1827.

<sup>4</sup> *Chem. Gaz.*, 1847, 357.

<sup>5</sup> *Am. J. Sci.*, [2], 3, 22, 1847.

Loewenberg<sup>1</sup> considered that legumin, as previously prepared, contained albumin and devised a method for the separation of these two proteids and gave analyses of the substances so prepared from almonds and peas.

Liebig<sup>2</sup> obtained plant casein (legumin) from beans, lentils, and peas, and gave an account of the properties of this proteid and two analyses. He concluded that the substance was identical in properties and composition with milk casein.

Dumas and Cahours<sup>3</sup> prepared legumin from peas, lentils, beans, almonds, plums, filberts, and white mustard. They considered all these seeds to contain the same proteid substance; that obtained from the three first named seeds being less pure than that from the others and therefore containing somewhat less nitrogen.

They gave analyses of preparations from all these seeds and an extended account of the properties of legumin, based on a study of the preparation obtained from the almond.

Contrary to Liebig, they concluded that this substance is not identical either with milk casein or plant casein. The latter designation they applied to the body which separates out on cooling a concentrated hot alcoholic extract of wheat gluten.

Rochleder<sup>4</sup> pointed out that the substance obtained from beans, lentils, and peas by Liebig was different from that of the almond described by Dumas and Cahours, and that for this reason these investigators did not reach the same conclusions. Rochleder prepared and analyzed legumin from two varieties of beans.

In 1868 Ritthausen undertook a study of legumin, the results of which are recorded in a series of papers whose publication extended over a period of fifteen years.<sup>5</sup>

He recognized that the seeds of almonds, plums, filberts, and white mustard, which had been previously stated to yield legumin, really contain a different proteid, which he called *conglutin*.

<sup>1</sup> *Ann. Phys.*, Pogg., 78, 327.

<sup>2</sup> *Ann. d. Chem. u. Pharm.*, 39, 138.

<sup>3</sup> *J. prakt. Chem.*, 28, 398.

<sup>4</sup> *Ann. d. Chem. u. Pharm.*, 46, 155.

<sup>5</sup> *J. prakt. Chem.*, 103, 65, 1868: *Die Eiweisskörper*, etc., Bonn., 1872: *Pflüger's Archiv.*, 15, 269, 1877: *Ibid.*, 16, 293, 1878: *Ibid.*, 18, 236, 1881: *J. prakt. Chem.*, [2], 24, 221, 1882: *Ibid.*, [2], 26, 504, 1882.

Up to this time legumin was considered to be the proteid that is extracted from seeds with water and is precipitated by acids from the aqueous extract.

All proteids thus obtained had been regarded as identical by most investigators and were known either as legumin or plant casein. Although it had been suggested that different seeds yield different proteids, Ritthausen appears to have been the first to make this fact evident. Ritthausen prepared "legumin" from blue lupins, yellow, green, and gray field peas, yellow garden peas, lentils, vetches, horse beans (*Vicia faba*), white and yellow beans (*Phaseolus*) and colza cake. The proteid of *Phaseolus*, Ritthausen afterwards found to be distinct from legumin, and one of us has, in the main, confirmed his later result and has named the proteid phaseolin.<sup>1</sup> Ritthausen afterwards considered the proteid which he obtained from colza cake to be an impure preparation of a different substance. His early analyses<sup>2</sup> of preparations from the leguminous seeds were fairly accordant, but he afterwards found that the soda lime method which was used in determining nitrogen gave too low results. He thereupon determined nitrogen anew by Dumas' method, and published a revised statement of the mean composition of legumin.<sup>3</sup>

In another paper published shortly afterwards, Ritthausen withdrew the corrected figures for nitrogen, having found that they were too high, because the nitrogen of his later analyses was mixed with hydrogen. He therefore published a third set of figures for nitrogen and made a second revised statement of the mean composition of legumin.<sup>4</sup>

At this time Hoppe-Seyler<sup>5</sup> and Th. Weyl<sup>6</sup> stated that the proteids of plants are chiefly globulins and Weyl examined qualitatively a number of seeds, by extracting then with ten per cent. sodium chloride solution, and found proteids resembling in their reactions animal myosin and vitellin. They asserted

<sup>1</sup> Report of the Conn. Agricultural Experiment Station, 1893, p. 186. and *This Journal*, 16, 633.

<sup>2</sup> *Die Eiweisskörper*, etc., Bonn., 1872. pp. 159, 176.

<sup>3</sup> Pflüger, *Archiv.*, 16, 293, 1877.

<sup>4</sup> Pflüger, *Archiv.*, 18, 236, 1878.

<sup>5</sup> *Physiol. Chemie.*, p. 75.

<sup>6</sup> *Ztschr. phys. Chem.*, 1, 72.

that the substance called legumin by Ritthausen was doubtless originally a globulin and that the preparations of this substance described and analyzed by him were altered by the alkali which he used in extracting them and were not the proteids originally contained in the seeds. Ritthausen contended strongly against this view and maintained that his preparations were wholly unaltered by the alkali. He extracted several kinds of seeds with salt solution, precipitated the proteid by dilution with water and found that the preparations of legumin so made were not essentially different in composition from those obtained by extracting with dilute potash water.<sup>1</sup> He then examined his older preparations, made by extracting the seeds with weak alkali and showed that they were to a very considerable extent soluble in salt solution. The substance thus extracted had, in many cases, a different composition from that of the original preparation, and Ritthausen then concluded that all the preparations which he had previously described as legumin were, in fact, mixtures of the two proteids, one, soluble in salt solution after dissolving in potash water and precipitating with acid, similar to, but distinct from conglutin, and the other originally soluble in salt solution but rendered insoluble in that fluid by treatment with alkalies. This latter he called legumin.

He then purified the legumin by extracting the mixed proteids from the seed with dilute alkali, neutralizing with acid, extracting the precipitate so produced with sodium chloride solution to remove proteids soluble in that fluid and then redissolving the residue, consisting mostly of legumin, in dilute alkali and reprecipitating with acetic acid.

Two preparations were so obtained, one from the pea and another from the horse bean (*Vicia faba*).

Ritthausen regarded his study of these preparations as showing that the substance from *Vicia faba* was a compound of tannic acid with the salt soluble proteid and that it was doubtful whether the horse bean contains legumin at all.

The preparation from the pea he finally considered to be legumin, having the following composition :

<sup>1</sup> *J. prakt. Chem.*, 26, 504.

## LEGUMIN OF PEA, RITTHAUSEN.

Carbon .....	51.34
Hydrogen .....	6.98
Nitrogen .....	17.48
Sulphur .....	0.45
Oxygen .....	22.75
	<hr/>
	100.00

This analysis represents the composition of legumin not in its original condition, but so altered as to be insoluble in saline solutions. Of the reactions of legumin we know little more than that it dissolves in salt solution and is precipitated by diluting with water.

In the following pages we give the outcome of our recent investigation into the composition and properties of legumin as contained in the seeds of the pea and the vetch.

Here, as in former papers, we have described our procedure with considerable, perhaps unnecessary, detail, but having often experienced great difficulty in understanding and repeating the work of our predecessors because of the vagueness of their statements, we have endeavored to describe our methods and results so fully and accurately that any who may wish to review our investigations experimentally may find it practicable to do so.

## I. PROTEIDS OF THE PEA.

One hundred grams of garden peas ground to pass a sieve of one mm. mesh were extracted with petroleum naphtha to remove oil, then dried by exposure to the air, and finally treated with one liter of ten per cent. sodium chloride solution. As the very viscid extract could scarcely be filtered through paper, an equal volume of ten per cent. sodium chloride solution was added, and after some time one-half the solution passed the filter clear. This was saturated with ammonium sulphate, the resulting precipitate was filtered out, dissolved in salt solution, and the liquid dialyzed free from chlorides. The proteid separated, as do all vegetable globulins thus far observed, in spheroids. No distinct crystals could be detected in this or any of our preparations from the pea. When the chloride had been removed by dialysis the precipitate was filtered out, washed with water and alcohol, dried over sulphuric acid, and found to weigh three

and a half grams, being about seven per cent. of the meal. Dried at 110° this preparation was analyzed with the following results :

## PEA LEGUMIN, 1.

Carbon .....	52.03
Hydrogen .....	6.96
Nitrogen .....	17.98
Sulphur .....	} 23.03
Oxygen .....	
	<hr/> 100.00
Ash .....	0.41

Another preparation was made by extracting 500 grams of pea meal with three liters of ten per cent. sodium chloride brine and after allowing the mixture, protected with thymol, to stand three days in a cool place, 1500 cc. of the extract were decanted. Although very turbid, this was saturated with ammonium sulphate without filtering, and the precipitate produced was filtered out and dissolved in brine. The resulting solution was then filtered without much trouble and the clear filtrate dialyzed free from chlorides. After washing and drying the globulin thus precipitated, and amounting to ten grams or about five per cent. of the meal, had the following composition :

## PEA LEGUMIN, 2.

	I.	II.	Average.
Carbon .....	52.08	52.19	52.14
Hydrogen .....	7.06	6.95	7.01
Nitrogen .....	18.01	17.91	17.96
Sulphur .....	0.49	....	0.49
Oxygen .....	....	....	22.40
			<hr/> 100.00
Ash .....	0.33		

In order to obtain larger quantities of this proteid for fractional precipitations 800 grams of pea meal were treated with four liters of *twenty* per cent. sodium chloride solution, and by draining on filters over night about one-half the solution applied to the meal, or two liters, was obtained as a clear yellow filtrate, which was saturated with ammonium sulphate, but for a reason, then unknown, very little proteid separated. Dilute acetic acid saturated with ammonium sulphate was then added in small



amount and the proteid separated as a flocculent precipitate. This was filtered out and in order to remove the acid as completely as possible the precipitate was suspended in about four liters of saturated ammonium sulphate solution and again filtered out. The precipitate was then dissolved in ten per cent. sodium chloride solution and calcium carbonate added to neutralize the acid retained by the proteid. The solution then reacted alkaline with litmus owing to ammonium carbonate set free from the sulphate. The solution was next filtered very nearly clear and dialyzed until a large precipitate had formed. This precipitate was filtered out, dissolved in salt solution, filtered clear and dialyzed free from chlorides. The precipitated globulin was washed with water and alcohol and dried over sulphuric acid, giving fifty-two grams, in whose analysis, after drying at  $110^{\circ}$ , the following figures were obtained :

## PEA LEGUMIN, 3.

	I.	II.	Average.
Carbon .....	52.30	52.27	52.29
Hydrogen.....	7.06	6.98	7.02
Nitrogen.....	17.72	17.79	17.76
Sulphur .....	0.30	....	0.30
Oxygen.....	....	....	22.63
			100.00

Ash..... 0.53

The solution filtered from this substance after its first precipitation by dialysis was saturated with ammonium sulphate, the resulting precipitate filtered out and dissolved in a little water, filtered clear and dialyzed. After removing the greater part of the salts by dialysis the precipitated globulin was filtered out, treated in the usual manner, and gave 14.2 grams of preparation 4, having, when dried at  $110^{\circ}$ , the following composition:

## PEA PROTEID, 4.

	I.	II.	Average.
Carbon .....	52.50	....	52.50
Hydrogen.....	6.74	....	6.74
Nitrogen.....	16.83	16.76	16.80
Sulphur .....	0.49	....	0.49
Oxygen .....	....	....	23.73
			100.00

Ash..... 0.33

Preparation 3, when dissolved in ten per cent. salt solution, was found to become turbid at 97° and after long heating in a boiling water-bath slowly developed a coagulum. Preparation 4 contained a considerable quantity of proteid coagulating at a much lower temperature. It was accordingly dissolved, as far as possible, in a little ten per cent. salt solution and the insoluble matter filtered out. The clear filtrate was diluted with distilled water until the solution contained 0.66 per cent. of salt, when a not inconsiderable precipitate formed, which was filtered out and the filtrate saturated with ammonium sulphate. This produced a relatively abundant precipitate, which was filtered out and dissolved in water. This solution, on heating, became turbid at 52°, and on keeping for some time at this temperature a minute quantity of flocks separated. Filtered at 56°, turbidity occurred again at 62° and a few flocks formed at 66°. Filtered at 67°, the solution became turbid at 70°, the turbidity increasing above 75° to a heavy flocculent coagulum at 79°.

It is evident from these results that we have in preparation 4 at least two proteids, one coagulating at 79°, the other being only slowly and imperfectly coagulated at 99°-100°; the former is readily soluble in very dilute salt solutions, the latter only slightly soluble in solutions containing less than one per cent. of salt. The filtrate from preparation 4 was dialyzed in water, but as no more globulin separated, the dialyzer was transferred to alcohol and the proteid thus completely thrown down. After washing with absolute alcohol and drying over sulphuric acid 12.31 grams of substance were obtained. This, of course, was a mixture of all the proteids extracted from the pea which had not been precipitated by dialysis in water. It was therefore treated with two per cent. salt solution, a large quantity of proteid which had been coagulated by the alcohol was filtered out, washed with water, with dilute and absolute alcohol, and dried over sulphuric acid. This preparation, 5, weighed 7.45 grams, and gave the following results when analyzed, after drying at 110°

## PEA PROTEID, 5.

	I.	II.	Average.
Carbon.....	53.40	53.26	53.33
Hydrogen.....	6.92	7.03	6.98
Nitrogen.....	16.19	16.09	16.14
Sulphur.....	1.00	....	1.00
Oxygen.....	....	....	22.55
			<hr/>
			100.00
Ash.....			0.32

The filtrate from 5 was saturated with ammonium sulphate, whereupon a small gummy precipitate appeared which was filtered out and dissolved in a small quantity of water. This solution when heated became turbid at 49° and flocculent at 60°; filtered at 75°, turbidity occurred on heating again to 72° and flocks formed at 79°. After heating to about 90° no more proteid was coagulated by boiling. The solution now contained a very small quantity of proteose.

Since acetic acid was used to separate the substance, from which 3, 4 and 5 were obtained, from the ammonium sulphate solution, it was necessary to obtain more of the proteids without the use of acid. It was found that the incomplete precipitation by ammonium sulphate was due to the use of twenty per cent. sodium chloride solution, in which less ammonium sulphate dissolves than in a ten per cent. salt solution, not enough, in fact, to completely precipitate the proteid. The meal residue was therefore treated with water enough to reduce the strength of the salt solution still adhering to it to about ten per cent. A further considerable quantity of nearly clear extract was thus obtained, which, when saturated with ammonium sulphate, readily and completely parted with the proteid. This was filtered out, dissolved in ten per cent. brine, the solution filtered perfectly clear and dialyzed. After a large quantity of globulin had separated in the dialyzer its contents were filtered off, the precipitate was dissolved in ten per cent. salt solution and treated in exactly the same way as 3 had been. This preparation, 6, weighed 37.5 grams and, dried at 110°, had the following composition :

## PEA LÉGUMIN, 6.

	I.	II.	Average.
Carbon.....	52.37	....	52.37
Hydrogen.....	6.90	....	6.90
Nitrogen.....	17.95	17.95	17.95
Sulphur .....	0.39	....	0.39
Oxygen.....	....	....	22.39
			<hr/>
			100.00
Ash.....	0.28		

The filtrate from the first precipitation, by dialysis, of this substance, when saturated with ammonium sulphate gave a precipitate which was dissolved in a little water and the resulting solution was filtered clear and dialyzed. After most of the salts were thus removed the separated globulin was filtered out, washed and dried, and gave 2.44 grams of preparation 7, having the following composition, when dried at 110°:

## PEA PROTEID, 7.

	I.	II.	Average.
Carbon .....	52.09	52.02	52.06
Hydrogen .....	6.96	7.08	7.02
Nitrogen .....	16.75	16.57	16.66
Sulphur .....	0.55	....	0.55
Oxygen.....	....	....	23.71
			<hr/>
			100.00
Ash.....	0.20		

This analysis is in fair accord with that of the similarly obtained preparation 4.

The filtrate from 7 was dialyzed into alcohol and then absolute alcohol was added to the solution until all the proteids separated. The precipitate thus produced was filtered out, washed with absolute alcohol, dried over sulphuric acid and found to weigh 7.1 grams. Since this preparation might be a mixture of any unprecipitated globulin, with albumin and proteose, if these were present, it was treated with water and the considerable quantity of proteid coagulated by alcohol was filtered out, washed thoroughly with water and then with absolute alcohol and dried over sulphuric acid. This gave 4.05 grams of preparation 8, which, when dried at 110°, had the following composition:

## PEA PROTEID, 8.

	I.	II.	Average.
Carbon .....	53.60	53.47	53.54
Hydrogen .....	6.99	6.98	6.99
Nitrogen .....	16.72	16.65	16.69
Sulphur .....	1.01	....	1.01
Oxygen .....	....	....	21.77
			<hr/> 100.00
Ash .....	0.32		

The analysis of 8 agrees well with that of 5 and it is probable that these figures pretty nearly represent the composition of a second proteid (globulin or albumin) readily soluble in very dilute salt solutions.

Having thus found evidence of the presence of at least two proteids in the pea extract, one less soluble than the other in very dilute salt solutions, it became necessary to subject the less soluble and more abundant globulin to thorough fractioning in order to learn whether it was homogeneous or a mixture.

Twenty-five grams of 3 were therefore dissolved in 250 cc. of five per cent. sodium chloride solution, filtered clear and the filter washed with fifty cc. of the same salt solution. A portion of the preparation had, as is usually the case with vegetable globulins when dried, passed into an insoluble form. This insoluble matter when treated with salt solution gave a gummy residue, which was difficult to filter out. No estimate of the amount of this substance could be made.

The clear salt solution of the globulin was diluted with twice its volume of water, making 750 cc. of a 1.67 per cent. solution of sodium chloride. After standing over night the proteid which had precipitated on dilution was collected on a filter, washed with water and alcohol and dried over sulphuric acid. Preparation 9 was so obtained, weighing five and one tenth grams and having, when dried at 110°, the composition given below.

The solution filtered from this substance was treated with an equal volume of water making 1500 cc. of a brine containing 0.84 per cent. of salt, from which after standing some time a part of the proteid separated as a viscid layer at the bottom of the beaker. The solution was decanted and the precipitate

washed and dried in the usual manner. This, 10, weighed 5.29 grams. The decanted liquid was then dialyzed free from salt and the precipitated globulin treated in the usual manner, giving 11, weighing 4.10 grams. About three-fifths of the original substance was thus recovered in three nearly equal fractions. The other two-fifths consisted largely of insoluble globulin. The composition of the fractions so obtained was as follows :

## PEA LEGUMIN, FRACTIONS OF 3.

	9.			10.			11.		
	I.	II.	Average.	I.	II.	Average.	I.	II.	Average.
Carbon ..	52.49	52.23	52.36	52.31	52.09	52.20	52.25	52.25	52.25
Hydrogen	7.11	7.10	7.11	7.09	6.92	7.01	7.08	....	7.08
Nitrogen.	17.96	18.05	18.01	17.98	17.96	17.97	17.88	17.84	17.86
Sulphur..	0.35	....	0.35	0.35	....	0.35	....	....	} 22.81
Oxygen ..	....	....	22.17	....	....	22.47	....	....	
			100.00			100.00			100.00
Ash .....			0.22			0.61			0.20

Again, twenty-five grams of preparation 6 were dissolved in 250 cc. of five per cent. brine, the solution filtered, the residue washed with fifty cc. of the same brine and the clear filtrate diluted with one and a half volumes of water, thus giving a two per cent. salt solution. After standing over night the precipitate was filtered out, washed with water and alcohol and dried over sulphuric acid. Preparation 12 so obtained weighed 8.58 grams.

The filtrate from 12, on adding an equal volume of water and treating the precipitate as just described, yielded 13, weighing 2.84 grams.

The filtrate from 13, dialyzed free from salt, gave 14, weighing four and two tenths grams.

## PEA LEGUMIN, FRACTIONS OF 6.

	12.			13.		14.		
	I.	II.	Average.	I.	II.	I.	II.	Average.
Carbon.....	52.26	....	52.26	52.08	52.01	52.02	52.02	52.02
Hydrogen.....	6.96	....	6.96	7.04	....	7.20	7.20	7.20
Nitrogen.....	17.96	18.06	18.01	17.88	17.81	18.03	17.92	
Sulphur .....	0.44	....	0.44	} 23.00	....	....	....	} 23.86
Oxygen.....	....	....	22.33		....	....	....	
			100.00		100.00			100.00
Ash.....			0.40		0.19			0.17

Comparing the analyses of these fractions with each other and with that of the original substance, it is plain that they all represent a single proteid.

## SUMMARY OF ANALYSES OF PEA LEGUMIN.

	I.	2.	3.	6.	9.	10.	11.
Carbon.....	52.03	52.14	52.29	52.37	52.36	52.20	52.25
Hydrogen..	6.96	7.01	7.02	6.90	7.11	7.01	7.08
Nitrogen...	17.98	17.96	17.76	17.95	18.01	17.97	17.86
Sulphur.. }	23.03	0.49	0.30	0.39	0.35	0.35	22.81
Oxygen .. }	22.40	22.63	22.39	22.17	22.47		
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

	12.	13.	14.	Average.
Carbon.....	52.26	52.08	52.02	52.20
Hydrogen..	6.96	7.04	7.20	7.03
Nitrogen...	18.01	17.88	17.92	17.93
Sulphur ... }	0.44	23.00	22.86	22.45
Oxygen .... }	22.33			
	100.00	100.00	100.00	100.00

Ritthausen obtained from peas by extraction with salt solution and precipitation with water two preparations, the analyses of which are given below, A and B.<sup>1</sup>

By treating peas with very weak potash water, adding acid to neutralization, extracting the precipitate thus produced with salt solution and filtering out the insoluble matter, he obtained a solution from which, by adding water, a precipitate was thrown down whose composition is given below under C.

## PEA LEGUMIN.

	Ritthausen.			Osborne & Campbell. Average of 18 analyses on 10 preparations.
	A.	B.	C.	
Carbon.....	52.83	51.61	51.62	52.20
Hydrogen.....	7.27	7.08	6.96	7.03
Nitrogen.....	17.26	17.23	18.26	17.90
Sulphur .....	22.64	24.08	0.33	0.39
Oxygen .....			22.83	22.48
	100.00	100.00	100.00	100.00

Ritthausen's preparation C agrees fairly well with the average of our results. The preparations extracted directly from peas

<sup>1</sup>*J. prakt. Chem.*, 26, 504.

by salt solution would appear to be the same substance but less pure. We see no ground for Ritthausen's idea that his older preparations were mixtures of two proteids both originally soluble in salt solution, one of which, legumin, is rendered insoluble in salt solution by treatment with alkalis. It is much more probable that a part of the globulin in his preparations had assumed the insoluble condition during the process of separating since nearly all globulins, to a greater or less extent, are prone to this change. The difference in composition between Ritthausen's original "legumin" and the substance extracted from it by salt solution is doubtless due to the greater purity of the latter. This view is supported by the close agreement in composition of this substance with those extracted by us directly from the pea. For this, the chief proteid of the pea, it is proper to retain the name *Legumin* first proposed by Braconnot.

The properties of legumin are as follows:

In water it is entirely insoluble.

In ten per cent. sodium chloride solution, when freshly prepared and not dried, it is readily soluble, but after washing with alcohol and drying over sulphuric acid, more or less becomes insoluble in salt solution. Dissolved in ten per cent. sodium chloride solution legumin is not precipitated by saturating the solution with magnesium sulphate, or sodium chloride. Saturated with sodium sulphate at 20°, no precipitate is produced; saturated at 25°, a turbidity appears; but saturated with sodium sulphate at 34°, all but a trace is thrown out of solution. By saturation with ammonium sulphate at common temperatures it is completely precipitated.

Dissolved in salt solution, legumin is not precipitated by mercuric chloride but gives a heavy precipitate on adding either picric, tannic, hydrochloric, nitric, sulphuric, or acetic acid.

In water containing a very small quantity of acid, legumin readily dissolves and is precipitated by adding sodium chloride. It is readily soluble in dilute alkalis and alkali carbonates.

Adding to its solution glacial acetic acid and concentrated sulphuric acid, a violet color is produced. With cupric sulphate and caustic potash, after standing, a crimson red color appears, almost as red as that given by peptones. With Mil-



lon's and the xantoprotein tests the usual reactions are given. When dissolved in ten per cent. sodium chloride solution and gradually heated, the solution becomes turbid at  $97^{\circ}$  and on long heating in a boiling water-bath, a coagulum gradually separates.

## II. PROTEIDS OF THE VETCH.

One hundred grams of finely ground meal of the seed of the common vetch (*Vicia sativa*) were treated with water and the extract, after filtering clear, was saturated with ammonium sulphate. The small precipitate thereby produced was filtered out and dissolved in water; the resulting solution was filtered clear and dialyzed until free from chlorides. The globulin thus precipitated, after washing with water and with alcohol, weighed 1.04 grams. The meal residue was then treated repeatedly with ten per cent. sodium chloride solution and after filtering clear the extract was saturated with ammonium sulphate, the precipitated proteid filtered out and dissolved in brine. The resulting solution was filtered clear and dialyzed until free from chlorides. The globulin thus precipitated, when washed with water and alcohol, and dried over sulphuric acid, weighed five grams. When dried at  $110^{\circ}$  this preparation, 15, had the following composition :

### VETCH LEGUMIN, 15.

Carbon .....	52.45
Hydrogen.....	6.98
Nitrogen .....	18.04
Sulphur.....	0.50
Oxygen .....	22.03
	<hr/>
	100.00
Ash .....	0.27

The meal residue was next treated with two-tenths per cent. potash water, the extract filtered clear and neutralized with very dilute hydrochloric acid; the precipitate thus produced was dissolved in two-tenths per cent. potash water, the clear solution was neutralized with dilute hydrochloric acid and the precipitated proteid washed with water and alcohol and dried. This preparation, 16, weighed four and four-tenths grams and gave the following results on analysis :

## VETCH PROTEID, 16.

	I	II.	Average.
Carbon .....	52.43	52.43	52.42
Hydrogen .....	7.13	7.02	7.07
Nitrogen .....	16.55	....	16.55
Sulphur .....	} ....	....	23.96
Oxygen .....			
<hr/>			100.00
Ash .....			0.74

Four kilograms of vetch meal were next treated with twelve liters of ten per cent. sodium chloride brine and the residue washed with the same solution. The extract and washings were partly cleared by subsidence, then saturated with ammonium sulphate. The precipitate so produced was dissolved in brine, but the resulting solution was very difficult to filter. The greater part of the suspended impurities was removed by passing the extract through a loose bed of filter paper pulp and the proteid was again separated by saturation with ammonium sulphate. This precipitate was dissolved in brine and the solution, kept cold, then filtered perfectly clear. This solution was dialyzed in two portions, D and E. After nearly freeing from chlorides, a large precipitate formed in each dialyzer, which was filtered out. That obtained from E was washed with water and with alcohol as long as any coloring matter was extracted, and was then dried over sulphuric acid giving 120 grams of a slightly pink powder, which will be designated F. That from D was redissolved in ten per cent. sodium chloride brine, the solution filtered perfectly clear and dialyzed until free from chlorides. All but a trace of proteid was thus thrown down. The precipitate was washed thoroughly with water and with alcohol and dried over sulphuric acid, yielding preparation 17, which weighed ninety grams and was very slightly colored. After drying at 110°, this preparation had the following composition :

## VETCH LEGUMIN, 17

	I.	II.	Average.
Carbon .....	51.98	51.97	51.98
Hydrogen .....	6.94	6.89	6.92
Nitrogen .....	17.96	18.00	17.98
Sulphur .....	0.45	....	0.45
Oxygen .....	....	....	22.67
<hr/>			100.00
Ash .....			0.20

The filtrates from the first dialysis of solutions D and E were separately saturated with ammonium sulphate, the precipitates obtained were dissolved in water and the solutions filtered and dialyzed. The precipitate from D, thrown down by dialysis, was redissolved in salt solution and again precipitated by dialysis. The two preparations of globulin thus obtained were washed with water and with alcohol and dried over sulphuric acid, that from D weighed 4.11 grams, forming preparation 18, and that from E gave preparation 19, weighing 7.67 grams. On analyzing these preparations, dried at 110°, the following results were obtained :

## VETCH LEGUMIN.

	18.	19.
Carbon .....	52.21	52.18
Hydrogen .....	6.82	6.82
Nitrogen .....	17.99	17.99
Sulphur .....	0.37	0.36
Oxygen .....	22.61	22.65
	<hr/>	<hr/>
	100.00	100.00
Ash .....	0.23	0.12

The filtrate from the first precipitation by dialysis of 18 was united with the filtrate from 19 and the heat coagulation point determined in a portion of the solution, in which ten per cent. of sodium chloride had been dissolved. This solution became turbid at 56° and flocks separated at 63° in considerable quantity. After heating to 70° for some time and filtering, turbidity occurred on heating to 71° and a flocculent coagulum formed at 73°, about the same in amount as at 63°. After heating to 78° the solution was filtered and again heated, the turbidity forming a third time at 79° and flocks at 83° in smaller quantity than before. This slow and incomplete coagulation does not necessarily indicate the presence of several coagulable proteids in the solution, for there is no temperature interval between the successive coagula, the temperature at which turbidity occurs and a flocculent coagulum develops being determined, after the first coagulum has formed, by the temperature at which the solution was filtered. Each time the solution becomes turbid at a temperature just above that to which it had been previously heated and a flocculent coagulum separates at three or four degrees higher.

The presence of salts has much influence on the coagulation point, for another portion of this same solution, to which no salt had been added, became turbid at ten degrees lower than the portion wherein ten per cent. of sodium chloride had been dissolved and gave the last flocculent coagulum at a temperature ten degrees higher.

The solution, portions of which had served for the foregoing observations, was then dialyzed into alcohol until concentrated to one-half its original volume, when a considerable precipitate formed, which was filtered out, washed with alcohol, and dried over sulphuric acid. This substance consisted of a mixture of all the proteids remaining in solution after separating the globulin, as described. Any albumin or globulin which might be contained in this precipitate would probably be largely if not wholly coagulated by the long treatment with alcohol and the subsequent drying. This preparation was therefore very finely pulverized and extracted thoroughly with water. The insoluble residue was then washed with alcohol and dried, yielding 13.52 grams of preparation 20, which was found to have the following composition :

VETCH PROTEID 20.			
	I.	II.	Average.
Carbon .....	53.45	53.65	53.55
Hydrogen .....	6.67	6.73	6.70
Nitrogen .....	16.46	....	16.46
Sulphur .....	1.02	....	1.02
Oxygen .....	....	....	22.27
			<hr/>
Ash .....	0.29		100.00

The solution filtered from 20 was further dialyzed into alcohol and a second precipitate obtained, which, when washed with alcohol and dried, weighed 5.64 grams, and was composed as follows :

VETCH PROTEID, 21.			
	I.	II.	Average.
Carbon .....	52.55	52.66	52.60
Hydrogen .....	6.70	6.95	6.83
Nitrogen .....	16.53	16.76	16.69
Sulphur .....	1.23	....	1.23
Oxygen .....	....	....	22.65
			<hr/>
Ash .....	0.65		100.00

The filtrate from the precipitate produced by the first dialysis into alcohol, from which preparations 20 and 21 had been obtained, was further dialyzed into alcohol yielding a second precipitate which, when washed with alcohol and dried over sulphuric acid, weighed 2.21 grams and formed preparation 22. This consisted of proteose and, after drying at  $110^{\circ}$ , had the composition as follows :

## VETCH PROTEOSE, 22.

	I.	II.	Average.
Carbon .....	50.95	50.76	50.85
Hydrogen.....	6.78	6.72	6.75
Nitrogen.....	16.53	16.79	16.65
Sulphur.....	} ....	} ....	25.75
Oxygen .....			
	<hr/>		<hr/>
			100.00
Ash.....	2.18		

Comparing the composition of 21 with that of 20, it is seen that, excepting carbon, the figures agree quite well. 21, however, contains one per cent. less carbon than 20, which is easily explained by its being a mixture of the proteose represented by 22, and the proteid represented by 20. Such a mixture would be expected from the method of preparation.

If 20 is compared with 5 and 8, obtained in a similar manner from the pea, by dialysis of its extracts into alcohol, after precipitation of the greater part of the globulin contained in these extracts by dialysis in running water, it will be observed that they agree rather closely. It is hardly possible by this method to obtain entirely pure preparations, but our results show that the vetch and pea both contain another proteid that is different from legumin in composition and in properties.

To facilitate comparison these analyses are here tabulated.

	Pea proteid.		Vetch proteid.
	5.	8.	20.
Carbon .....	53.33	53.54	53.55
Hydrogen .....	6.93	6.99	6.70
Nitrogen.....	16.14	16.69	16.46
Sulphur .....	1.00	1.01	1.02
Oxygen.....	22.55	21.77	22.27
		100.00	100.00

It will be noted that this proteid contains more carbon and less nitrogen than legumin and nearly twice as much sulphur.

Whether it is a globulin soluble in extremely dilute salt solution or an albumin soluble in pure water, we have not as yet undertaken to ascertain, for want of time.

The residue of the meal extracted, as described, with salt solution, was treated with two-tenths per cent. potash solution, a portion of the alkali extract was filtered clear and neutralized with very dilute hydrochloric acid. The precipitate which resulted was dissolved in two-tenths per cent. potash water, and after filtering perfectly clear, again thrown down by neutralizing with hydrochloric acid. After drying 12.4 grams of 23 were obtained, having the following composition :

VETCH PROTEID, 23.			
	I.	II.	Average.
Carbon .....	53.00	52.99	53.00
Hydrogen.....	6.91	7.02	6.97
Nitrogen.....	16.45	....	16.45
Sulphur .....	0.53	....	0.53
Oxygen.....	....	....	23.05
			<hr/> 100.00
Ash.....	0.92		

If this analysis is compared with that of 16, it will be noted that, although they agree in nitrogen content, they differ as respects carbon. The sulphur found in 23 would indicate that 23 is a mixture of legumin with other substances. It seems to us probable that it is mainly legumin which escaped extraction by the salt solution through imperfect pulverization of the meal or its incomplete exhaustion by the brine, or because it was present in the salt-insoluble form, a form which it may have assumed in the seed itself, or under the action of the solvents to which the meal was subjected. It has been our experience with other seeds that extractions with alkali, after exhausting the seed with salt solution, yields products which, in most cases, it is impossible to purify.

In order next to determine whether the legumin found in the vetch seed is a single proteid or a mixture, the following fractional precipitations were made.

One kilogram of the meal was extracted with ten per cent.

sodium chloride solution and, after filtering clear, the extract was saturated with ammonium sulphate and the proteids, thus precipitated, dissolved in 300 cc. of ten per cent. brine. The solution now measured 400 cc. and contained about eight per cent. of salt. After filtering perfectly clear, from a small amount of insoluble matter, an equal volume of distilled water was added. On standing a short time the proteid thus precipitated collected on the sides and bottom of the beaker as a sticky deposit, leaving the solution nearly clear. The latter was then decanted and the translucent, gummy mass of proteid washed with water, which caused it to turn opaque and become brittle, so that it was easily rubbed to a coarse powder.

After washing repeatedly with water the proteid was thoroughly washed with dilute alcohol, then with absolute alcohol, and dried over sulphuric acid. The preparation, 24, weighed 13.4 grams.

The solution decanted from 24 was cooled in an ice box over night and the clear supernatant liquid poured from the perfectly transparent semifluid layer which had thus formed on the bottom of the beaker. After washing and drying, 12.9 grams of preparation 25 were obtained. The solution decanted from 25 was mixed with an equal volume of distilled water and left over night in the ice box. A transparent layer of proteid was again deposited, which, when washed and dried, yielded 4.00 grams of 26.

The solution decanted from 26 was saturated with ammonium sulphate, the precipitated proteid dissolved in salt solution, and after filtering, the proteid was precipitated by dialysis. The globulin thus separated, after washing and drying, weighed 3.35 grams, and formed preparation 27.

The following figures were obtained by analyzing these preparations when dried at 110°.

VETCH LEGUMIN.				
	24.	25.	26.	27.
Carbon.....	52.05	51.78	52.17	52.04
Hydrogen .....	6.99	6.89	6.92	7.06
Nitrogen .....	18.02	18.06	17.70	18.02
Sulphur.....	0.56	0.48	23.21	22.88
Oxygen .....	22.38	22.79		
	100.00	100.00	100.00	100.00

Several grams of preparation E, described on page 598, were dissolved in a little two-tenths per cent. potash water, the solution was diluted considerably with distilled water and carbon dioxide passed through it. At first the solution remained clear, but after a time the proteid suddenly and almost completely separated as a voluminous precipitate, the filtrate from which yielded but a trace of proteid on saturating with ammonium sulphate. The precipitate was washed with water and then treated with salt solution. A part dissolved and the rest was converted into a swollen gelatinous mass which rendered filtration impossible. After standing over night the solution was poured off and the gummy residue was washed by decantation, at first with salt solution and then with water. On washing out the salt, the residue lost its gummy character and became a dense, rapidly settling precipitate which was readily collected on a filter and completely washed with water and then with alcohol. After drying over sulphuric acid it furnished 2.62 grams of preparation 28. This peculiar behavior of legumin which has lost its solubility in salt solution, we have observed in a number of cases.

E, when treated directly with salt solution, behaved in exactly the same manner as the precipitate obtained by passing carbon dioxide through its solution in dilute potash water, that is, a part dissolved and a part remained as a gummy residue, which was dehydrated (?) by washing with water. The saline solution described above, which had been decanted from the part of the carbon dioxide precipitate which was insoluble in salt solution, was filtered clear and dialyzed free from chlorides. The precipitate which resulted was filtered out, washed and dried in the usual manner, and yielded 29. These two preparations were found to have the following composition :

## VETCH LEGUMIN.

	28.	29.
Carbon .....	52.11	51.89
Hydrogen .....	6.82	6.88
Nitrogen .....	18.17	18.09
Sulphur .....	0.53	0.40
Oxygen .....	22.37	22.74
	<hr/>	<hr/>
	100.00	100.00
Ash .....	0.27	0.13



Several grams of preparation 17 was dissolved in a little two-tenths per cent. potash water and the resulting clear solution was neutralized with dilute acetic acid, thereby precipitating the proteid. A portion of this precipitate was tested with ten per cent. sodium chloride solution and found to dissolve to a large extent and on warming to 50° nearly all went into solution. The remainder of the precipitate was washed, dried and analyzed with the following results :

## VETCH LEGUMIN, 30.

Carbon .....	52.06
Hydrogen .....	6.80
Nitrogen .....	17.98
Sulphur .....	0.53
Oxygen .....	22.63
	<hr/>
	100.00
Ash .....	0.15

Another portion of preparation 17 was dissolved in a little two-tenths per cent. hydrochloric acid and yielded a clear solution, which was neutralized with one-half per cent. sodium carbonate solution. The resulting precipitate was partly soluble in ten per cent. salt solution. It was washed and dried and, as preparation 31, gave the following figures when analyzed :

## VETCH LEGUMIN, 31.

Carbon .....	52.12
Hydrogen .....	6.68
Nitrogen .....	18.20
Sulphur .....	0.40
Oxygen .....	22.60
	<hr/>
	100.00
Ash .....	0.15

For convenience of comparison the analyses of legumin from the vetch are brought together in the following tables :

## SUMMARY OF ANALYSES OF VETCH LEGUMIN.

	15.	16.	18.	19.	24.	25.
Carbon .....	52.45	51.98	52.21	52.18	52.05	51.78
Hydrogen ..	6.98	6.92	6.82	6.82	6.99	6.89
Nitrogen ....	18.04	17.98	17.99	17.99	18.02	18.06
Sulphur .....	0.50	0.45	0.37	0.36	0.56	0.48
Oxygen .....	22.03	22.67	22.61	22.65	22.38	22.79
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00	100.00	100.00

	26.	27.	28.	29.	30.	31.
Carbon .....	52.17	52.04	52.11	51.89	52.06	52.12
Hydrogen ...	6.92	7.06	6.82	6.88	6.80	6.68
Nitrogen ....	17.70	18.02	18.17	18.09	17.98	18.20
Sulphur . . }	23.21	22.88	0.53	0.40	0.53	0.40
Oxygen.... }			22.37	22.74	22.63	22.60
	100.00	100.00	100.00	100.00	100.00	100.00

It will be seen from the following statement that the composition of legumin from the pea is identical with that from the vetch.

#### LEGUMIN.

	Pea. Average of 18 analyses on 10 preparations.	Vetch. Average of 13 analyses on 12 preparations.
Carbon .....	52.20	52.09
Hydrogen .....	7.03	6.88
Nitrogen.....	17.93	18.02
Sulphur .....	0.39	0.46
Oxygen.....	22.45	22.55
	100.00	100.00

What we have already stated concerning the properties and reactions of pea legumin applies strictly to that from the vetch except in two particulars. The solutions of pea legumin in ten per cent. brine when heated nearly to boiling become turbid and, after a time, a considerable coagulum separates in the form of a semi-solid clot. Similar solutions of the vetch legumin, on the other hand, remain perfectly clear, even after prolonged boiling.

Many carefully conducted experiments made with the legumin from each of these seeds, wherein the same quantity of globulin was dissolved in the same amount of salt solution of the same strength, were carried out side by side, but always with the same results, the pea legumin coagulating to a greater or less extent while the vetch legumin remained wholly unaffected.

That this difference is due to some foreign substance is indicated by the following experiment: A quantity of ten per cent. sodium chloride extract of pea meal was filtered clear and divided into two parts, one of which was dialyzed directly, the

other was saturated with sodium chloride and filtered clear. The latter solution was less viscid and much more easily filtered, presumably due to the removal of gum. This solution, saturated with salt, was then dialyzed.

The globulin precipitated by dialysis from each of the above named solutions, was dissolved in brine to new solutions containing ten per cent. of globulin and eight per cent. of sodium chloride. When these two solutions were heated, side by side, in the same water-bath and for the some length of time, a most marked difference was observed in the quantities of coagulum that appeared. Each solution contained a small quantity of the proteid coagulating at about  $80^{\circ}$ , so that after being heated to  $85^{\circ}$  for some time, they were filtered clear and again heated.

Each solution then became turbid at  $93^{\circ}$  and, after heating the bath to boiling for a little time, the solution of the globulin from the salt saturated extract became curdy, from the separation of a moderate quantity of coagulum, while that from the unsaturated extract set to a firm opaque jelly, so that the tube could be inverted without displacement of its contents.

The second difference noted was very slight, but appeared to be constant. By precipitating the legumin from the pea by dialysis, the proteid was obtained in the form of spheroids which showed little tendency to adhere in masses, while that from the vetch was always obtained in more or less coherent lumps which, however, were not at all fluid and gummy, but were easily broken up on stirring. In our opinion, the legumin from these two seeds is one and the same substance, or must, at least for the present, be so regarded.

#### SUMMARY.

1. So far as we have investigated, peas and vetches contain the same proteids, which are nearly if not entirely soluble in ten per cent. sodium chloride solution.

2. The greater part of these proteids consists of a globulin, the *Legumin* of Braconnot, which is readily precipitated by dialyzing its salt solutions.

The prevalent idea that legumin is soluble only in acids and alkalies is erroneous, it having been proved, notably by Ritt-

hausen, to be a true globulin. The composition of legumin, as shown by the average of our accordant analyses of thirty-one preparations obtained from the seeds of peas and vetches, is the following :

## LEGUMIN.

Carbon.....	52.15
Hydrogen.....	6.96
Nitrogen.....	17.98
Sulphur.....	0.43
Oxygen.....	22.48
	<hr/>
	100.00

Legumin is abundantly soluble in solutions containing above five per cent. of sodium chloride ; in those containing less salt it is not so soluble, the amount held in solution decreasing as the salt content diminishes, so that it is but sparingly soluble in solutions containing less than one per cent. of salt. By dilution with water, strong saline solutions of legumin are abundantly precipitated.

By saturation with sodium chloride or magnesium sulphate, its sodium chloride solutions are not precipitated ; by saturation with sodium sulphate at 25° they are not precipitated, but at higher temperatures more or less is thrown down, and by saturation with sodium sulphate at 34°, precipitation is very nearly complete. With nitric acid, Millon's and Adamkiewicz's reagents it gives the usual proteid reactions.

With strong solutions of legumin the biuret test gives a violet color at first, which on standing becomes crimson red, similar to the color produced by peptones.

The legumin obtained by us from the vetch is not coagulated by heat nor even rendered turbid by prolonged boiling of strong solutions.

The legumin prepared by us from the pea is partly coagulated by heating strong solutions in a boiling water-bath, and sets to a firm jelly after thus heating for some time. These differences in their behavior on heating, and a greater tendency of the vetch legumin to cohere in semi-solid lumps when precipitated by dialysis, are the only points, of dissimilarity which a rigid comparison of preparations from the two seeds has revealed.

These differences, in our opinion, are due to the substances with which the proteid is associated in the two seeds, for saturation of the pea extracts with sodium chloride, before precipitating the legumin by dialysis, greatly diminished the amount of coagulum given by the pea legumin.

3. Besides the legumin, the pea and vetch contain another proteid in small amount, either an albumin or a globulin, soluble in extremely dilute salt solutions, and coagulated by heating its solutions to 80°. This substance we have not studied further than to make two preparations for analysis from the pea and one from the vetch. These were obtained in an insoluble form by coagulating with alcohol, so that the properties and reactions were not determined. The composition of this proteid is shown by the following average of three closely agreeing analyses :

PROTEID OF PEA AND VETCH.

Carbon.....	53.48
Hydrogen .....	6.89
Nitrogen .....	16.43
Sulphur.....	1.01
Oxygen .....	22.19
	<hr/>
	100.00

4. In addition to the foregoing proteids a very little *protease* was found in the extracts of both these seeds.

5. No attempt has yet been made to determine the total quantity of proteids in these seeds, nor to study minutely the proteids that occur in them in small proportion.

## CONGLUTIN AND VITELLIN.<sup>1</sup>

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received May 21, 1896.

REVIEW of the literature relating to the plant proteids hitherto described as conglutin and vitellin, shows that the subject is in great confusion, which can only be cleared up by a thorough examination of the seeds from which these proteids are said to have been obtained. This is the more important, because of late years various investigations have been made in

<sup>1</sup>From the Report of the Connecticut Agricultural Experiment Station for 1895. Communicated by the authors.

which these proteids have figured as the subject of study, while the fact, that the purity or even the identity of the proteid employed is very doubtful, has been entirely overlooked or ignored. Thus the results of observations on the globulin of lupins have been applied to the globulin of the squash, hemp and other seeds, it being apparently unknown that these two proteids are very distinct substances. Further, the composition and reactions of most of these bodies have never been adequately studied, nor the means of preparing them in a state of purity ascertained. Recent authors are mostly content to call these proteids vegetable vitellin and to assume, with little reason, that the proteid from the many seeds in which vitellin has been said to occur is one and the same substance. With the object of determining, so far as may be practicable, the true relations of the globulins found in the various seeds hitherto alleged to contain conglutin and vitellin, this investigation was undertaken.

#### ALMOMDS.

The proteid first discovered, which has since been known as conglutin, was found in the seed of the almond by Proust,<sup>1</sup> and by him named amandin.

Dumas and Cahours<sup>2</sup> described and analyzed preparations obtained from almonds, peach and plum seeds, and considered them to be legumin, identical with that of a large number of other seeds.

According to Rochleder<sup>3</sup> the proteid described by Dumas and Cahours is different from legumin as understood by Liebig and others. Norton<sup>4</sup> analyzed proteid preparations which he obtained from the almond and considered them to be legumin. Ritthausen<sup>5</sup> described the proteid of the almond under the name conglutin. He later<sup>6</sup> obtained from the peach kernel a proteid which he considered to be conglutin, identical with that of almonds and lupins.

The details of our investigation are as follows: A quantity of

<sup>1</sup> *J. de phys., de chim., d'histoire naturelle et des arts*, 54, 199.

<sup>2</sup> *J. prakt. Chem.*, 28, 398.

<sup>3</sup> *Ann. der Chem. u. Pharm.*, 46, 155.

<sup>4</sup> *Am. J. Sci.*, [2], 5, 22.

<sup>5</sup> *Eiweisskörper*, Bonn, 1872.

<sup>6</sup> *J. prakt. Chem.*, 26, 422, 1882.

sweet almond meats deprived of the brown skin (tegmen) were crushed and treated with ether to remove oil. Seventy-five grams of the oil-free meal was then extracted with ten per cent. sodium chloride solution, the extract was filtered clear and dialyzed until free from chlorides. The globulin separated at first in minute spheroids, which, on settling to the bottom of the dialyzer, united, forming a viscid semi-fluid translucent mass of a pale straw color. After decanting the solution, the globulin, which had separated, was again dissolved in ten per cent. sodium chloride brine and reprecipitated by dialysis. The proteid, obtained in the same condition as before, was washed with water, and with alcohol, dilute at first and afterwards gradually increased in strength, and finally was dehydrated with absolute alcohol and dried over sulphuric acid. This preparation, 1, weighed 6.72 grams, was a snow white, dense powder, and, after drying at 110°, gave the following results on analysis :

## AMANDIN, I.

				Average.
Carbon.....	51.49	51.32	....	51.41
Hydrogen.....	7.33 <sup>1</sup>	6.86	....	6.86
Nitrogen.....	19.29	19.52	19.62	19.47
Sulphur.....	0.39	....	....	0.39
Oxygen.....	....	....	....	21.87
				<hr/>
Ash.....	0.24			100.00

Another preparation of this globulin was made by crushing a quantity of fresh, shelled, "Jordan almonds," and extracting the oil with petroleum naphtha. After freeing from naphtha, the greater part of the skins was separated by sifting. 100 grams of the meal was then extracted with one liter of water and the solution filtered and saturated with ammonium sulphate. The precipitate produced was filtered out, dissolved in water, the resulting solution filtered perfectly clear and dialyzed until free from chlorides. The proteid, which on dialysis deposited with the same appearance and characters as the first preparation, was washed with water, dilute alcohol, stronger alcohol and then dehydrated with absolute alcohol and dried over sulphuric acid.

<sup>1</sup> Omitted in average.

Sixteen grams were obtained, equal to sixteen per cent. of the meal. This preparation, owing to the seed-integument, which had been but partly removed, was somewhat red in color. After drying at  $110^{\circ}$ , analysis gave the following results :

AMANDIN, 2.			
			Average.
Carbon .....	51.49	....	51.49
Hydrogen .....	6.85	....	6.85
Nitrogen .....	19.27	19.05	19.16
Sulphur .....	0.44	....	0.44
Oxygen .....	....	....	22.06
			<hr/>
Ash .....	0.80		100.00

For a third preparation Jordan almonds were drenched with hot water for a moment to loosen the skins, which were then easily detached ; the meats were squeezed in a drug press to separate the greater part of the oil. The remainder of the oil, after dehydrating the pressed meats with absolute alcohol, was extracted with naphtha. The residue was freed from naphtha by evaporation and ground to a fine powder. There was thus obtained from 900 grams of almonds 380 grams of oil-free meal. This was thoroughly extracted with ten per cent. sodium chloride brine and the extract filtered. A turbid liquid resulted which was saturated with ammonium sulphate. The proteid thus precipitated was dissolved in ten per cent. sodium chloride brine and the solution after filtering perfectly clear was dialyzed until nearly free from chlorides. The solution was then decanted from the semi-fluid, viscid precipitate which had formed, and this was washed with water and alcohol, dehydrated with absolute alcohol and dried over sulphuric acid. The proteid thus obtained weighed sixty-six grams. The filtrate from this preparation was saturated with ammonium sulphate, the precipitate was filtered out, dissolved in a little water and the filtered solution was dialyzed. This second dialysis yielded twenty-seven grams more of globulin which were added to that before obtained, making in all ninety-three grams, being twenty-four and one-half per cent. of the oil-free meal. Analysis of this preparation, 3, dried at  $110^{\circ}$ , gave results as follows :



AMANDIN, 3.				Average.
Carbon .....	51.18	....	....	51.18
Hydrogen .....	6.99	....	....	6.99
Nitrogen .....	19.30	19.37	....	19.33
Sulphur .....	0.48	....	....	0.48
Oxygen.....	....	....	....	22.02
				<hr/>
Ash.....	0.35			100.00

A portion of 3 was dissolved in sodium chloride solution and dialyzed into dilute alcohol in the hope of obtaining the globulin in the form of crystals. No distinct crystals resulted, and after remaining about two weeks in alcohol the precipitated proteid was readily redissolved in salt solution, not having been coagulated by the alcohol, and the clear solution was dialyzed in water until free from chlorides. After washing and drying in the usual manner this preparation, 4, was analyzed :

AMANDIN, 4.					Average.
		I.	II.		
Carbon ...	51.39	51.32	51.36	51.36	
Hydrogen .....	6.99	6.90	6.95	6.95	
Nitrogen .....	19.32	19.36	19.34	19.34	
Sulphur .....	0.45	....	0.45	0.45	
Oxygen.....	....	....	21.90	21.90	
				<hr/>	100.00
Ash.....	0.20				

#### PEACH KERNEL.

Ritthausen states that peach seeds contain the same proteid as the almond, a fact in harmony with the close botanical relations of the two plants.

We obtained this proteid from peach pits in the following manner : The seeds were freed from the skin (tegmen) by cutting it away with a knife and were then ground with ether to a powder and freed from oil. Only a small quantity of seeds, yielding but twenty grams of oil-free meal, were at the time available. This was extracted with ten per cent. sodium chloride solution and the clear filtered extract dialyzed. The globulin separated in spheroids, which settled to a translucent viscid semi-fluid mass like that from the almonds. The solution, when freed from chlorides

by dialysis, was decanted from the precipitate and the latter was washed with water, alcohol and absolute alcohol and dried over sulphuric acid; 2.44 grams or 12.2 per cent. of the meal were so obtained. Analysis of this preparation gave the following results:

AMANDIN, FROM THE PEACH, 5.			Average.
Carbon .....	51.06	51.02	51.04
Hydrogen .....	6.86	6.79	6.83
Nitrogen .....	19.20	19.35	19.28
Sulphur .....	0.48	....	0.48
Oxygen .....	....	....	22.37
			100.00
Ash .....	0.62		

Owing to the small quantity of 5, it was not possible to compare its reactions throughout with those of amandin from the almond, but, so far as could be observed, the two were identical in all respects, and there can be no doubt that they are the same substance.

In the following table the foregoing results may be compared with those obtained by earlier investigators, in their work upon the proteid of the almond, peach and plum:

AMANDIN.						
	Dumas and Cahours.		Löwenburg.		Norton.	
	Almonds.	Plums.	Almonds.		Almonds.	
Carbon .....	50.89	50.93	51.10	50.50	50.97	49.16
Hydrogen ...	6.71	6.73	7.20	6.56	6.64	6.51
Nitrogen ....	18.93	18.64	....	17.33	17.15	17.43
Sulphur .....	....	....	....	0.32	0.27	0.41
Phosphorus..	....	....	....	1.05	0.57	2.21
Oxygen .....	23.47	23.70	....	24.24	24.40	24.27
		100.00		100.00	100.00	100.00
Ritthausen.						
			Almonds		Peach.	
Carbon .....			50.44		50.82	
Hydrogen .....			6.85		6.94	
Nitrogen .....			18.61		18.60	
Sulphur .....			0.43		0.32	
Oxygen .....			23.67		23.32	
			100.00		100.00	

## AMANDIN.

	Osborne and Campbell, Almonds.				Peach.	
	1	2	3	4	5	Average.
Carbon .....	51.41	51.49	51.18	51.36	51.04	51.30
Hydrogen ...	6.86	6.85	6.99	6.95	6.83	6.90
Nitrogen ....	19.47	19.16	19.33	19.34	19.28	19.32
Sulphur .....	0.39	0.44	0.48	0.45	0.44	0.44
Oxygen .....	21.87	22.06	22.02	21.90	22.37	22.04
	100.00	100.00	100.00	100.00	100.00	100.00

Amandin, that has been dried over sulphuric acid, when mixed with cold water dissolves to a very slight extent and forms a gummy plastic mass. In water heated to about 98° amandin melts to a transparent mass and a considerable portion goes into solution, which in part separates out on cooling, and is redissolved on heating again. Boiling the solution causes but a slight turbidity.

The precipitate formed by cooling the hot water solution of amandin, dissolves completely on addition of a little nitric acid, but if more nitric acid be added, a precipitate falls which dissolves on warming and reappears on cooling in exactly the manner of a proteose.

In ten per cent. sodium chloride solution this proteid dissolves readily to a slightly opalescent liquid, no insoluble "albuminate" being formed by drying, as is the case with most vegetable globulins.

A solution containing ten per cent. of amandin dissolved in ten per cent. sodium chloride brine gives an abundant precipitate when poured into much distilled water, but if only a small amount of proteid is dissolved in the brine no precipitate is produced by dilution.

Salt solution of amandin is not precipitated by saturating with sodium chloride. By saturating with magnesium sulphate it is partly thrown down. Saturation with sodium sulphate or ammonium sulphate completely precipitates it.

Nitric acid added to the sodium chloride solution forms a precipitate soluble in an excess of acid which, on heating, gives the usual xanthoprotein reaction.

With mercuric chloride solution no precipitate is formed.

With picric acid and also with tannic acid heavy precipitates are produced.

Amandin is readily soluble in very dilute acetic acid. The acetic solution yields an abundant precipitate with potassium ferrocyanide that is difficultly soluble in an excess of this salt to a solution precipitable by diluting with water. In concentrated glycerol the dry proteid dissolves quite readily, the clear solution yielding a considerable precipitate on adding absolute alcohol.

Concentrated hydrochloric acid dissolves it, with development of a violet-blue color on standing. By heating in quite dilute sulphuric acid a solution is obtained which becomes turbid on cooling, the proteid being far less soluble in sulphuric than in hydrochloric or acetic acids. With the biuret test and also with glacial acetic acid and concentrated sulphuric acid together, solutions of this globulin give a fine violet color.

After solution in very dilute potash water and precipitation by neutralizing with acetic acid, amandin retains its original solubility in salt solutions.

A ten per cent. sodium chloride solution, containing five per cent. of amandin, becomes turbid when heated to 75°, and at 80° flocks form in small quantity which slowly increase on gradually raising the temperature, but only a small part of the proteid is coagulated even by boiling.

Having thus, as we believe, established this proteid as a chemical species quite distinct from all others hitherto investigated, it is proper to restore the designation *Amandin* given it by Proust, its discoverer, and to discard for it the names vitellin and conglutin, which are associated with many erroneous statements as to its occurrence, composition and characters.

#### WALNUT, (*Juglans regia*).

Ritthausen<sup>1</sup> prepared the proteid from this seed, but owing to the large amount of tannin present in the skins, he found much difficulty in obtaining satisfactory results.

As Ritthausen's preparations differed widely in composition,

<sup>1</sup>J. prakt. Chem., 24, 257.

and as he has published nothing respecting the properties of this proteid, we have made several preparations with the following results.

A quantity of walnut meats was crushed, freed from oil by extracting with petroleum naphtha, and the greater part of the skins removed by sifting. One hundred grams of this meal was then extracted with ten per cent. sodium chloride brine and, after filtering, eight-tenths of the salt solution applied was recovered as a clear extract corresponding to about eighty grams of meal. This was saturated with ammonium sulphate and the resulting precipitate filtered out and treated with salt solution. Much that failed to dissolve was separated by filtration and the clear solution was dialyzed until free from chlorides. During dialysis the proteid was deposited in spheroids which did not like amandin, unite to a confluent mass. The precipitated globulin was then filtered out, washed with water, alcohol and absolute alcohol and dried over sulphuric acid. Only 2.87 grams was obtained, equal to about 3.6 per cent. of the meal. This small yield was undoubtedly due to tannin, which rendered the greater part of the proteid insoluble in salt solution.

Dried at  $110^{\circ}$  this preparation, 6, had the following composition:

## WALNUT GLOBULIN, CORYLIN, 6.

			Average.
Carbon .....	50.32	50.32	50.32
Hydrogen.....	6.63	6.74	6.69
Nitrogen....	19.06	19.12	19.09
Sulphur .....	....	....	23.90
Oxygen .....	....	....	
<hr/>			<hr/>
Ash .....	0.63		100.00

The part of the ammonium sulphate precipitate which was not taken up by salt solution at  $20^{\circ}$  was treated with brine at  $60^{\circ}$ . In this it dissolved almost completely and did not precipitate on cooling. The clear filtered solution was dialyzed free from chlorides, and by the usual process, 2.82 grams or 3.5 per cent. of globulin was obtained, having the following composition:

## WALNUT GLOBULIN, CORYLIN, 7.

Carbon.....	50.83	
Hydrogen.....	6.79	
Nitrogen.....	19.05	19.04
Sulphur .....	0.89	
Oxygen .....	22.44	
	<hr/>	
	100.00	
Ash.....	0.15	

In order to avoid the presence of tannin, another lot of walnut seeds were drenched for a moment with hot water, whereupon the skins were easily stripped off. The crushed meats were then treated with ether to extract the oil and, after removal of ether by exposure to the air, the coarse meal was finely ground and fifty grams was extracted with 1500 cc. of ten per cent. brine of common salt. The extract was filtered clear, saturated with ammonium sulphate, the resulting precipitate dissolved in salt solution at 40° and the extract dialyzed free from chlorides. The precipitated globulin was then filtered out and treated in the usual manner, giving preparation 8, weighing ten grams, equal to twenty per cent. of the meal, and having the following composition :

## WALNUT GLOBULIN, CORYLIN, 8.

			Average.
Carbon .....	50.77	50.74	50.76
Hydrogen .....	6.94	6.83	6.89
Nitrogen .....	19.10	19.02	19.06
Sulphur .....	....	....	} 23.29
Oxygen .....	....	....	
			<hr/>
			100.00
Ash.....	0.32		

HAZEL-NUT OR FILBERT, (*Corylus tubulosa*).

Ritthausen<sup>1</sup> has detailed the results of his examination of the proteid of this seed and concluded it to be identical with the conglutin which he obtained from almonds.

In order to satisfy ourselves respecting this substance a quantity of hazel-nut meats was freed from skins and oil as already described in case of walnuts, and finely pulverized. The meal

<sup>1</sup>J. prakt. Chem., 24, 257.

was then extracted with ten per cent. sodium chloride brine and the filtered extract saturated with ammonium sulphate. The precipitated proteid was filtered out, dissolved in salt solution, and the liquid, after filtering clear, was dialyzed free from chlorides.

During dialysis the globulin separated in spheroids which, like those of walnut globulin, settled down, without adhering together to a plastic mass, after the manner of amandin. The precipitated globulin was filtered out and treated in the usual way. When dried at  $110^{\circ}$  this preparation had the following composition :

## CORVILIN, FILBERT GLOBULIN, 9.

			Average.
Carbon .....	50.64	50.86	50.72
Hydrogen .....	lost	6.86	6.86
Nitrogen.....	19.14	19.19	19.17
Sulphur .....	0.83	....	0.83
Oxygen.....	....	....	22.42
			<hr/> 100.00
Ash.....	0.28		

In properties this preparation exactly resembled the globulin obtained from the walnut. That the two are identical in composition is shown by the following statement :

## CORVILIN.

	Walnuts			Filberts.
	6	7	8	9
Carbon.....	50.32	50.83	50.76	50.72
Hydrogen.....	6.69	6.79	6.89	6.86
Nitrogen.....	19.09	19.05	19.06	19.17
Sulphur } .....	23.90	0.89 }	23.29	0.83
Oxygen }		22.44 }		22.42
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The properties of this proteid, after drying over sulphuric acid, as exhibited by preparations 8 and 9, are as follows. In the dry state it forms a heavy snow-white powder which, unlike amandin, is entirely insoluble in distilled water at  $20^{\circ}$  or at  $40^{\circ}$ . In ten per cent. sodium chloride solution it dissolves readily and completely, as also in exceedingly dilute acids and alkalies. Sulphuric acid, however, dissolves it much less readily than acetic, hydrochloric or nitric acid.

The solution in ten per cent. sodium chloride brine, containing ten per cent. of this globulin, gives an abundant precipitate when diluted with an equal volume of water. More dilute solutions give precipitates on sufficient dilution. Corylin is very much more readily precipitated by dilution than amandin. Hydrochloric acid and acetic acid each gives a precipitate insoluble in considerable excess of acid, when added to saline solutions of the proteid. With mercuric chloride, picric acid, or tannic acid dissolved in ten per cent. sodium chloride brine, heavy precipitates are produced. Saturation with sodium chloride gives a slight precipitate. Saturation with magnesium sulphate produces a considerable though partial precipitation. Saturation with sodium sulphate or ammonium sulphate effects a complete precipitation.

Dissolved in a little acetic acid, a precipitate is produced by sufficient nitric acid, which dissolves on heating and partly reprecipitates on cooling. The solution in acetic acid gives a precipitate with potassium ferrocyanide, but slightly soluble in a large excess of the latter.

With the biuret test the usual violet color is obtained. With Millon's and the xanthoprotein tests the ordinary proteid reactions appear. Dissolved in concentrated hydrochloric acid and boiled, a violet blue color develops on standing.

With glacial acetic acid and concentrated sulphuric acid, solutions of corylin give a violet color. When five per cent. of this proteid is dissolved in ten per cent. sodium chloride brine and the solution heated, turbidity ensues at about 80° and flocks form in small amount at 99°. On boiling the solution, a little more coagulates, but the corylin is precipitated by heat very slowly and incompletely.

When dissolved in dilute potash water and precipitated by neutralization, the proteid dissolves completely in ten per cent. salt solution. These reactions and the results of analysis show this body to be entirely distinct from either amandin or edestin. We therefore propose the name *Corylin*, from the generic name of the filbert, *Corylus tubulosa*, in which this proteid was first found by Dumas and Cahours.<sup>1</sup>

<sup>1</sup>*J. prakt. Chem.*, 28, 398.



BRAZIL-NUT, (*Bertholletia excelsa*).

Weyl<sup>1</sup> described the globulin of the Brazil-nut under the name of vegetable vitellin, and first determined its composition with a close approach to accuracy.

One of us has already investigated this substance as to its composition and properties, when prepared both in the form of spheroids and as perfectly distinct crystals.<sup>2</sup> This proteid, being evidently different from all others hitherto examined, deserves a distinct name, and we accordingly propose to designate it *Excelsin*.

## OAT-KERNEL.

From the oat-kernel one of us<sup>3</sup> obtained a crystallized globulin very similar in composition to excelsin, but different in its reactions as well as in crystalline form. This globulin might be classed as a vitellin, and for that reason is here referred to. As yet this proteid has received no specific name and we now propose to call it *Avenalin*.

HEMP, (*Cannabis sativa*), SQUASH, (*Cucurbita maxima*), AND CASTOR BEAN, (*Ricinus communis*)

Proteid preparations from the seeds of hemp, squash and castor bean have been described under the names of conglutin and vitellin. One of us<sup>4</sup> has shown that these seeds contain, as their chief and characteristic proteid, one and the same substance and has named it *Edestin*. This has been found in a larger number of seeds than any proteid yet discovered, and is the body most commonly called vegetable vitellin. It is readily obtained pure in octahedral crystals, from several seeds, and owing to this fact has been employed in physiological investigations. That it is a different substance from the proteids already described in this article appears to have been mostly overlooked. The properties and composition of edestin are detailed in the paper above mentioned, and in the annual reports of Connecticut Experiment Station for 1893, pp. 179, 214, 216, and 1894, pp. 155, 170, 190.

COCOANUT, (*Cocos nucifera*.)

The proteid of the cocoanut was examined by Ritthausen<sup>5</sup>

<sup>1</sup> *Ztschr. phys. Chem.* 1, 85.

<sup>2</sup> Osborne: *Am. Chem. J.*, 14, 662.

<sup>3</sup> Osborne: Reports of Connecticut Experiment Station 1890 and 1891, and *Am. Chem. J.*, 14, 212 and 682.

<sup>4</sup> Osborne: *Am. Chem. J.*, 14, 671-689.

<sup>5</sup> Pflüger's Archiv., 21, 96.

who, without identifying it with conglutin, assigned to it a similar composition. Chittenden<sup>1</sup> under the general name phytovitelin, gives the composition of this proteid in close accord with that of edestin, and as he obtained it partly crystallized in octahedra it probably is edestin.

#### LUPIN (*Lupinus*.)

The principal proteid contained in lupin seeds is the body to which Ritthausen first gave the name conglutin.<sup>2</sup> We have devoted much labor to the study of this proteid, but the results of our work are not yet complete and will form the subject of a future paper. We find that it is distinctly different in composition and properties from the proteids which we have hitherto noticed, and we take especial pleasure in confirming to it the name *conglutin* proposed by its veteran discoverer.

We give on the following page the composition of conglutin as found by us in accordant analyses of six preparations from the blue lupin.

#### SUNFLOWER (*Helianthus*.)

The proteid of the sunflower seed as described by Ritthausen<sup>3</sup> appears to be identical with edestin, but our investigation of this substance, which is still in progress, shows that the proteid prepared by the usual methods is contaminated with the helianthotannic acid described by Ludwig and Kromayer.<sup>4</sup> As yet we have been unable to obtain this proteid in the pure state.

To the best of our knowledge the proteids noticed in this paper include all which have been hitherto designated either as conglutin or vitellin. Of late years many seeds have been described as containing vitellin, but its presence has been inferred from qualitative reactions and not, except in those cases mentioned in this paper, from a study of the isolated proteid.

We have accordingly at least six perfectly distinct proteids which have been confounded together under the name vitellin or conglutin. The following table shows the present state of our knowledge concerning the composition of these globulins and sets forth the characters in which they have been found to differ.

<sup>1</sup> Medical Record, 45, 450, and Digestive Proteolysis, New Haven, 1895, p. 32.

<sup>2</sup> Eiweisskörper, Bonn, 1872, and *J. prakt. Chem.*, 25, 422.

<sup>3</sup> Pflüger's Archiv., 21, 81.

<sup>4</sup> N. Br. Arch., 99, 1 and 285.

PROTEIDS FORMERLY KNOWN AS VITELIN OR CONGLUTIN.

	Feculin.	Amandin.	Corylin.	Ricelutin.	Avenalin.	Conglutin.
Carbon.....	51.65	51.30	50.72	52.18	52.18	51.00
Hydrogen.....	6.89	6.90	6.86	6.92	7.05	6.90
Nitrogen.....	18.75	19.32	19.17	18.30	17.90	17.99
Sulphur.....	0.85	0.44	0.83	1.06	0.53	0.40
Oxygen.....	21.86	22.04	22.42	21.54	22.34	23.71
	100.00	100.00	100.00	100.00	100.00	100.00
Salt solution saturated with:						
Sodium chloride.	No pp.	No pp.	No pp.	No pp.	Complete pp.	No pp.
Magnesium sulphate.	Complete pp.	Partial pp.	Partial pp.	Slight pp.	Complete pp.	No pp.
Mercuric chloride.	Pp.	No pp.	Pp.	No pp.	Pp.	No pp.
Solution of ten per cent. proteid and ten per cent. sodium chloride diluted with equal volume of water gives:						
Heat coagulation:	Pp.	No pp.	Pp.	Slight pp.	Pp.	No pp.
Turbidity.	88°	75°	80°	70°	No coagulation even on boiling.	Trace of coagulation at 99° sets to jelly on cooling.
Flocks.	95°	80°	99°	84°	Spheroids, pulverulent.	Spheroids uniting to plastic mass.
Precipitate by dialysis:	Octahedral crystals or spheroids, pulverulent.	Spheroids, uniting to viscid fluid.	Spheroids, pulverulent.	Hexagonal plates or spheroids, pulverulent.	Spheroids, pulverulent.	Spheroids uniting to plastic mass.
Found in seeds of:	Hemp, Castor bean, Squash, Flax, Cotton, Wheat, Rye, Barley, Maize, Coconut.	Almond, Peach, Walnut, Filbert.	Brazil-nut.	Oat.	Lupin.	



Fig. 2. *Anhalonium Lewinii*.



Fig. 3. *Anhalonium Williamsii*.

among peoples more advanced in the scale of civilization, and have consequently been made the subject of some chemical investigation. Their fresh juices produce irritation of the skin when locally applied, and preparations of them are administered internally as cardiac stimulants and for other purposes. The first article published in this country on the subject seems to have been one by A. F. Pattee, which appeared in the *Boston Medical and Surgical Journal* in 1867. O. M. Meyers published an article in the *New York Medical Journal* in 1891, in which he called attention to the value as a heart tonic of a preparation of *Cereus grandiflorus* called "cactina." This was claimed to be the active principle of the drug, but it was not stated whether it was alkaloidal, glucosidal, or of some other nature. Numerous papers quickly followed, containing reports of clinical experiments with this and other preparations of the drug. Some of these papers included brief reports of chemical investigations. Boinet and Boy-Tessier reported the finding of an alkaloid in this species.<sup>1</sup> G. Sharp<sup>2</sup> stated that he was unable to find either alkaloid or glucoside in the drug, and ascribed any active properties that it may have to the resin that it contains. He failed to obtain any marked effect from the drug itself, and took doses of forty and one hundred of the cactus pills, prepared from *Cactus Mexicana*, without result. This is practically all that has been done in the way of chemical investigation of this class of plants in recent years, excepting the species that we are to consider and a few species closely related thereto.

As far as I have been able to learn, three groups of persons have been especially active in the scientific study of the *Cactaceae* during the last decade: First, a group of persons at Berlin, the center of which is Dr. L. Lewin, whose earlier work has been reported in this country in a pamphlet published by Parke, Davis & Co., of Detroit, and in the *Therapeutic Gazette* for 1888; second, a group of persons at the Pharmacological Institute of the University of Leipsic, where the work has been conducted by Dr. Arthur Heffter; third, a group of persons in this city, centering in the Bureau of American Ethnology, and including

<sup>1</sup> *Bulletin général de Thérapeutique*, 1891, 121, 343-349.

<sup>2</sup> *London Practitioner*, 1894.

as associates the Division of Chemistry of the Department of Agriculture for chemical studies, Drs. Prentiss and Morgan for the study of physiological properties, and the Botanical Division of the Department of Agriculture for the settlement of botanical questions. These more recent investigations have been directed toward one or more species of cacti that are used by the American Indians for ceremonial and medicinal purposes. This substance, known as "mescal buttons" in the commerce of our southwestern border and in Mexico as *peyote* or *pellote*, has been of commercial and medicinal importance in Mexico for many years, being mentioned by Spanish writers as early as 1790. It was included in the Mexican Pharmacopoeia of 1842, but has been omitted from the later editions. The species furnishing the "mescal buttons" is *Anhalonium Lewinii* (Hennings), for which the synonymous names are *Anhalonium Williamsii*, var., *Lewinii* and *Lophophora Williamsii*, var., *Lewinii*. There seems to be evidence that *Anhalonium Williamsii* also contributes to the supply of "mescal buttons" and *pellote*. This latter species is likewise burdened with an abundance of names, being known among botanists by the names of *Echinocactus Williamsii* and *Lophophora Williamsii*, in addition to the one just used to designate it.

For a detailed account of the use of the dried "buttons" by the Indians, I quote, by permission, from a recent article on the subject by Mr. James Mooney of the Bureau of American Ethnology:<sup>1</sup>

"About five years ago, while making investigations among the Kiowa Indians on behalf of the Bureau of Ethnology, the attention of the writer was directed to the ceremonial use of a plant for which were claimed wonderful medical and psychologic properties. So numerous and important are its medical applications, and so exhilarating and glorious its effect, according to the statements of the natives, that it is regarded as the vegetable incarnation of a deity, and the ceremonial eating of the plant has become the great religious rite of all the tribes of the southern plains. \* \* \* \* \*

<sup>1</sup> The Mescal Plant and Ceremony, by James Mooney. *Therapeutic Gazette*, January, 1896.

"As a matter of fact, there are several varieties, probably all of the same genus, used by the Indians in a ceremonial way. The explorer Lumholtz mentions three varieties among the Tarahumari of northern Mexico, (see his article in *Scribner's Magazine* for October, 1894). A different sort, from the lower Rio Grande, is used by the Kiowas and associated tribes, and a smaller variety is found among the Mescalero Apaches of eastern New Mexico. In each language it has a different name, usually referring to the prickles. Among the Kiowas it was *seni*; among the Comanches, *wokowi*; with the Mescaleros, *ho*; and with the Tarahumaris, *hikori*. The traders of the Indian Territory commonly call it mescal, although it must not be confounded with another mescal in Arizona, the *Agave*, from which the Apaches prepare an intoxicating drink. The local Mexican name upon the Rio Grande is *peyote* or *pellote*, from the old Aztec name *peyotl*.

"The use of the plant for medical and religious purposes is probably as ancient as the Indian occupancy of the region over which it grows. There is evidence that the ceremonial rite was known to all the tribes from the Arkansas to the valley of Mexico, and from the Sierra Madre to the coast. The Mescalero Apaches take their name from it. Personal inquiry among the Navajos and Mokis proved that they had no knowledge of it.

"In proportion as the plant was held sacred by the Indians, so it was regarded by the early missionaries as the direct invention of the devil, and the eating of the peyote was made a crime equal in enormity to the eating of human flesh. From the beginning it has been condemned without investigation, and even under the present system severe penalties have been threatened and inflicted against Indians using it or having it in their possession. Notwithstanding this, practically all the men of the Southern Plains tribes eat it habitually in the ceremony, and find no difficulty in procuring all they can pay for. In spite of its universal use and the constant assertion of the Indians that the plant is a valuable medicine and the ceremony a beautiful religious rite, no agency physician, post surgeon,

missionary, or teacher—with a single exception—has ever tested the plant or witnessed the ceremony.

"A detailed account of mythology, history and sacred ritual in connection with the mescal would fill a volume. Such an account, to be published eventually by the Bureau of Ethnology, the writer is now preparing, as the result of several years of field study among the Southern Plains tribes.

"The ceremony occupies from twelve to fourteen hours, beginning about nine or ten o'clock and lasting sometimes until nearly noon the next day. Saturday night is now the time usually selected, in deference to the white man's idea of Sunday as a sacred day and a day of rest. The worshippers sit in a circle around the inside of the sacred tipi, with a fire blazing in the center. The exercises open with a prayer by the leader, who then hands each man four mescals, which he takes and eats in quick succession, first plucking out the small tufts of down from the center. In eating, the dry mescal is first chewed in the mouth, then rolled into a large pellet between the hands, and swallowed, the man rubbing his breast and the back of his neck at the same time to aid the descent. After the first round the leader takes the rattle, while his assistants take the drum, and together they sing the first song four times, with full voices, at the same time beating the drum and shaking the rattle with all the strength of their arms. The drum and rattle are then handed to the next couple, and so the song goes on round and round the circle—with only a break for the baptismal ceremony at midnight, and another for the daylight ceremony—until perhaps nine o'clock the next morning. Then the instruments are passed out of the tipi, the sacred foods are eaten, and the ceremony is at an end. At midnight a vessel of water is passed around, and each takes a drink and sprinkles a few drops upon his head. Up to this hour no one has moved from his position, sitting cross-legged upon the ground and with no support for his back, but now any one is at liberty to go out and walk about for a while and return again. Few, however, do this, as it is considered a sign of weakness. The sacred food at the close of the ceremony consists of parched corn in sweetened water; rice or other boiled grain; boiled fruit, usually now prunes or





Fig. 4. *Anhalonium fissuratum*.

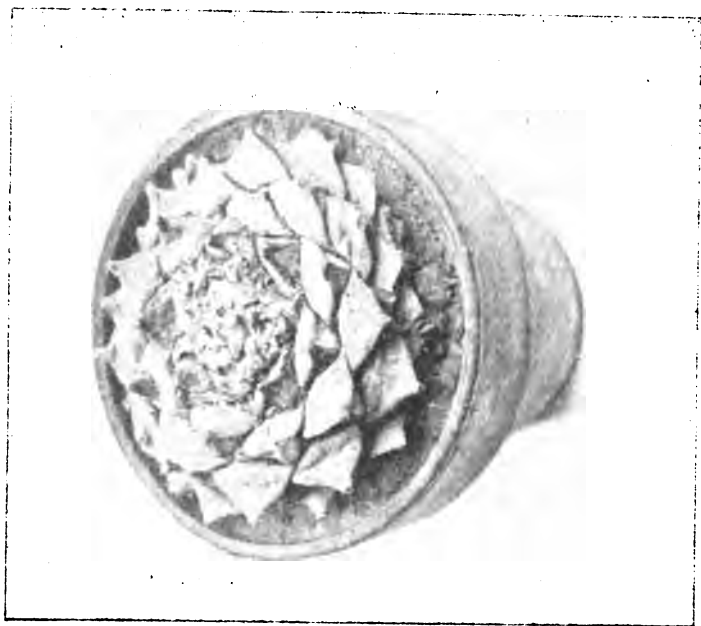


Fig. 5. *Anhalonium prismaticum*.

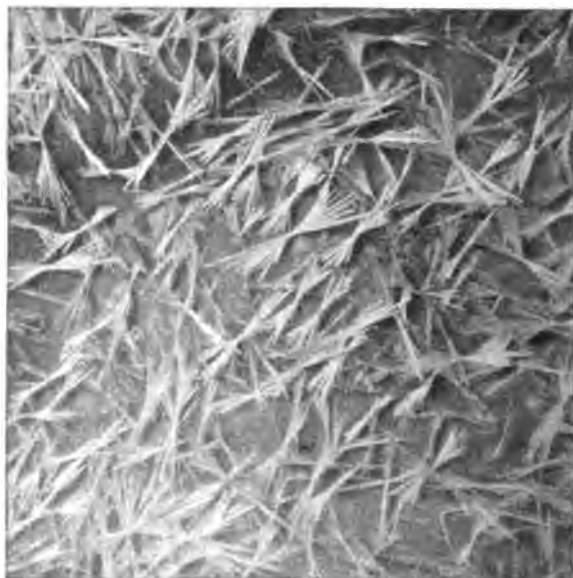


Fig. 6. Anhalonin hydrochlorate.



Fig. 7. Hydrochlorate of a new alkaloid separated from *Anhalonium Leuinit.* (Enlarged nine diameters.)

dried apples ; and dried meat pounded up with sugar. Every person takes a little of each, first taking a drink of water to clear his mouth.

"After midnight the leader passes the mescal around again, giving to each man as many as he may call for. On this second round I have frequently seen a man call for ten and eat them one after the other as rapidly as he could chew. They continue to eat at intervals until the close. There is much spitting, and probably but little of the juice is swallowed. Every one smokes hand-made cigarettes, the smoke being regarded as a sacred incense. At intervals some fervent devotee will break out into an earnest prayer, stretching his hands out toward the fire and the sacred mescal the while. For the rest of the time, when not singing the song and handling the drum or rattle with all his strength, he sits quietly with his blanket drawn about him and his eyes fixed upon the sacred mescal in the center, or perhaps with his eyes shut and apparently dozing. He must be instantly ready, however, when his turn comes at the song, or to make a prayer at the request of some one present, so that it is apparent that the senses are always on the alert and under control of the will.

"There is no preliminary preparation, such as by fasting or the sweat-bath, and supper is eaten as usual before going in. The dinner, which is given an hour or two after the ceremony, is always as elaborate a feast as the host can provide. The rest of the day is spent in gossiping, smoking, and singing the new songs, until it is time to return home. They go to bed at the usual time, and are generally up at the usual time the next morning. No salt is used in the food until the day after the ceremony.

"As a rule, only men take part in the regular ceremony, but sick women and children are brought in, and, after prayers for their recovery, are allowed to eat one or more mescals prepared for them by the priest."

It is to Mr. Mooney that we are indebted for the commencement of the scientific study of the drug in this country. On his return in the summer of 1894, from a prolonged residence among the tribes that use the drug, he brought with him a considerable

quantity of the dried "buttons" for use in scientific investigations. A portion of this material was turned over to Dr. H. W. Wiley, Chief of the Division of Chemistry of the Department of Agriculture, for a study of its chemical constituents. This task was assigned to the author by Dr. Wiley in September, 1894. The only literature of the subject at hand at that time was the article published by Dr. Lewin in 1888,<sup>1</sup> in which he announced the discovery and name, anhalonin, of an alkaloid in *Anhalonium Lewinii*, a name that had been given to the plant furnishing "mescal buttons" by Hennings, the botanist to whom Lewin intrusted the botanical identification of the crude material in which the alkaloid was found. Work had hardly been begun in the laboratory of the Department of Agriculture with the result of the separation of a considerable portion of Lewin's anhalonin, when Dr. Heffter<sup>2</sup> published an article in which he reported the results of a chemical study of four species of the genus *Anhalonium*: *A. fissuratum*, *A. prismaticum*, *A. Williamsii*, *A. Lewinii*. This was quickly followed by a report by Lewin of the continuation of his experiments mentioned above.<sup>3</sup>

For the aid of the American readers who may feel an interest in this subject, the writer has prepared the following table, in which the results of the investigations, hitherto reported, of the three more thoroughly studied species of anhalonium, are presented in a convenient form for reference and comparison:

<sup>1</sup> *Archiv für experimentelle Pathologie und Pharmacologie*, 1888, 24, 401; *Therapeutic Gazette*, 1888, p. 232, and in a pamphlet issued by Parke, Davis & Co., of Detroit, the same being a reprint from "The Pharmacology of the Newer Materia Medica."

<sup>2</sup> *Archiv für experimentelle Pathologie und Pharmacologie*, 1894, 34, 65-86.

<sup>3</sup> *Archiv für experimentelle Pathologie und Pharmacologie*, 1894, 34, 374-391.



Taste.	Aqueous solutions of the salts of this base have a bitter, saline taste, resembling that of potassium iodid.	Intensely and persistently bitter.					
Reactions with alkaloidal precipitants $KI + HgI_2$	A morphous precipitate.	A morphous precipitate, becoming short, thick prisms.	Snow-white, well-formed microscopic tables.	Citron-yellow, crystalline precipitate, composed of short needles grouped in clusters.			
$KI + BiI_3$	A morphous precipitate.	A morphous precipitate, becoming orange red, curved needles.	A morphous precipitate.	A morphous red-brown precipitate.			
$KI + CdI_2$			No precipitate.	No precipitate.	A precipitate is formed.		
$KI + I_2$	Brown drops separate, which solidify to prisms after a time.	A morphous precipitate, becoming bright brown, long, thin needles.	Very thin, long needles of a beautiful steel-blue color.	A morphous, fire-red precipitate.		Amorphous, brown-red precipitate.	Very small brown needles.
Phosphotungstic acid.	Amorphous precipitate.	A morphous precipitate.	A morphous precipitate.	Amorphous, yellow-white precipitate.		Crystalline, white precipitate.	Amorphous, white precipitate.

Phosphomolybdic acid. $\text{PtCl}_4$ .	Amorphous precipitate. No precipitate in aqueous solution; a precipitate separates in the form of drops from the alcoholic solution. The same as with $\text{PtCl}_4$ .	Amorphous precipitate. From weak alcoholic solution, forms golden yellow, fern-like aggregates of crystals.	Amorphous precipitate. Bright-yellow, low, fine needle-like, grouped in the form of sheaves. This precipitate is very insoluble in water.	No precipitate.	No precipitate.	Short, broad, obliquely cut prisms.	Flaky crystals at first shaking.	Amorphous, yellow precipitate. Bright-yellow, low precipitate, which arranges itself in clusters of crystals.	Amorphous, yellow precipitate. Amorphous, yellow-brown precipitate.
$\text{AuCl}_3$ .	No precipitate. The same as with $\text{PtCl}_4$ .	No precipitate. (?)	No precipitate.	No precipitate.	Precipitate.	Crystalline, brown, beautifully formed crystals.	Crystalline, brown precipitate.	Amorphous, brown precipitate.	Amorphous, brown precipitate.
$\text{HgCl}_2$ .	The same as with $\text{PtCl}_4$ .								
Picric acid.		Amorphous precipitate, becoming star-shaped groups of prismatic needles.	No precipitate.	No precipitate.	Precipitate.	Yellow, crystalline precipitate.	Bright-yellow, low, amorphous precipitate that becomes crystals on standing.	Amorphous, white precipitate. Bright-yellow, low, amorphous precipitate.	Amorphous, white precipitate. Bright-yellow, low, amorphous precipitate.
Tannic acid.		No precipitate.	No precipitate.	No precipitate.	No precipitate.	Yellowish-white, amorphous precipitate.	White, amorphous precipitate.		
$\text{AgNO}_3$ .							White, amorphous precipitate in solutions of the free base.		
$\text{K}_2\text{Cr}_2\text{O}_7$ .							In concentrated solution dendritic crystals are formed after some time.		Amorphous, brown-red precipitate.

$\text{FeCl}_3$						Immediately after the addition of the reagent there is formed a thick mass of yellow-white, long prismatic crystals. No precipitate.	No precipitate.
$\text{NH}_4\text{CNS}$ .							Amorphous, brown precipitate.
Color reactions. $\text{H}_2\text{SO}_4$ .	Quickly dissolves with no color in the cold or on heating.	Dissolves with a slight yellow color that is not altered by standing or warming.				Is colored yellow and on heating turns to a violet-red color that is very persistent.	Similar to anhalonin.
$\text{HCl}$ .	The same as with $\text{H}_2\text{SO}_4$ .						
$\text{H}_2\text{SO}_4 + \text{HNO}_3$ .	A drop of $\text{HNO}_3$ added to the $\text{H}_2\text{SO}_4$ solution produces a green color.	The crystal dissolves with a brown-red color that changes to an intense per-manganate color on warming.	The same as with pectolin.	The same as with pectolin.	A permanent color which turns yellow after some time.	A deep violet-red which soon becomes brown colorless.	
$\text{HNO}_3$ .		The same as with $\text{H}_2\text{SO}_4 + \text{HNO}_3$ .	The same as with $\text{H}_2\text{SO}_4 + \text{HNO}_3$ .			A light-red, then blood-red, which turns yellow on warming.	



<p><math>\text{HNO}_3</math> fol- lowed by <math>\text{KOH}</math></p>	<p>A small crys- tal warmed on the water-bath with one to two drops of <math>\text{HNO}_3</math> forms a yellow solution that is turned a per- sistent orange- red by an ex- cess of solu- tion of <math>\text{KOH}</math>.</p>					<p>Chlorin wa- ter turns an aqueous solu- tion light yel- low, on warm- ing this be- comes rose-red and changes to green on long standing.</p>	
<p><math>\text{Cl}_2</math>.</p>			<p>No crystal- lizable salt was obtained.</p>				
<p>SALTS.</p>							
<p>Hydrochlo- rate. Crystalline form.</p>	<p><math>\text{C}_{10}\text{H}_{17}\text{NOHCl}</math>.</p>			<p>On adding ether to the solution of the salt in absolute alcohol, small, shining, tabu- lar crystals were obtained.</p>	<p>Hard prism.</p>		
						<p>This salt crystallizes from the aque- ous solution more readily than the free base. It forms colorless, six- sided prisms of the rhombic system, 0.3-0.7 mm. broad and 3-7 mm. long. Their termina- tions are some- times pointed and sometimes basal planes.</p>	

Solubility.	Very readily soluble in water, alcohol, and methyl alcohol.	Very easily soluble in water.				Slightly soluble in cold water; easily soluble in hot water, forming a neutral solution: soluble in alcohol. Melts at 24-25° with decomposition. $[\alpha]_D^{25} = -40.56$ Concentration was 1.33 g/m <sup>2</sup> in 100 cc. of 50 per cent. alcohol. Slightly bitter.
Melting-point						
Specific rotatory power.						
Taste.						Very bitter.
Sulphate.	$(C_6H_5NO)_2 \cdot H_2SO_4 \cdot 2H_2O$					
Crystalline form.	Colorless, shining, very thin tablets which were obtained by crystallization from alcohol.	Not obtained in crystalline form.	Colorless, shining needles.	Small, white, non-lustrous, rhombic tablets.		
Solubility.	Very easily soluble in cold water; less readily soluble in cold alcohol but readily soluble in hot, ninety per cent alcohol.		Difficultly soluble in cold water; easily soluble in hot water; almost insoluble in alcohol.	More readily soluble in cold water than alkaloid "A."		

Melting-point	Melts without coloration at 197°.	169°.	220°.					
Oxalate.	(C <sub>10</sub> H <sub>7</sub> NO) <sub>2</sub> (COOH) <sub>2</sub> .							
Crystalline form.	Readily crystallized from hot alcohol in a form similar to that of the aniphatc.	Needles.						
Solubility.	Similar to anhalin sulphate.	Very easily soluble in cold water; insoluble in alcohol.						

All of the bases mentioned in the above table are possessed of marked physiological properties, and produce death when administered to the lower animals in sufficient doses. The nature and extent of the physiological activity of these alkaloids as determined by the experiments of Lewin and Heffter, are shown in the following table :



The nature of the action.	The action of this alkaloid has a narcotic effect upon frogs is effect when summed up as taken by men a paralysis of the central nervous system without preceding excitement, the hours after action appearing the entirely being drug into the limited to the brain.	0.05-0.06 gram	No increase of reflex excitability was observed.	No increase of reflex excitability was observed.	More active than either "Alkaloid A." or "Alkaloid B." or pelltin. Tetanic spasms with increased reflex excitability.	Tremors, tetanic spasms with opisthotonus, marked increase of reflex excitability. In the case of frogs, the animal remains for several days in such a condition that any slight exterior disturbance calls forth a series of tetanic convulsions.	Tetanic spasms with increase of reflex excitability, the latter apparently being less marked than in the case of the crystalline an-halonin hydrochlorate.
	In the case of rabbits, large doses produce muscular weakness, followed by tetanic spasm, with opisthotonus, increasing in intensity or followed by recovery according to the amount of the dose. There is increase of reflex excitability and the tetanic spasm can be produced by exterior disturbance. With frogs the tetanic condition may last three or four days.						

The materials used by Lewin in his experiments reported in 1894 were prepared in the laboratory of J. Merck & Co., of Darmstadt. In their report to Lewin, mention was made of the presence of still a third base in the drug, which forms a crystallizable hydrochlorate that is easily soluble in cold water. It seems quite possible that the substance described under the name of "amorphous anhalonin hydrochlorate" was a mixture of alkaloidal hydrochlorates.

Heffter also made a cursory examination of a small sample of *Anhalonium prismaticum* and found it to contain a small percentage of alkaloidal constituents possessing high physiological activity.

In the article published by Lewin, in 1894, and cited above, mention is made of a partial analysis of a sample of *Anhalonium Jourdanianum* made in 1889 with the result of the separation of an alkaloid that formed a crystalline hydrochlorate and resembled anhalonin in its characteristic color-reaction as well as the nature of its physiological action upon frogs. In the same article report is also made of an examination of *Anhalonium Williamsii*, several species of *Mammillaria*, and one species of *Opuntia*. The study of *A. Williamsii*, which was made in 1891, resulted in the separation of an alkaloid that caused an increase of reflex excitability, and marked tetanus when administered to frogs. The tendency of the tetanic condition to continue for several days was very pronounced. The milky juices yielded by *Mamillaria polythele*, *M. centricirrha* var. *pachythele*, *M. pulchra*, Haw. and *M. arietina*, were found to possess no poisonous properties. *Mammillaria uberiformis* was found to be poisonous. *Rhipsalis conferta*, a member of the *Opuntia* group, yielded a slimy juice that was difficultly soluble in water. When this was administered to frogs by hypodermic injection a paralysis of the voluntary muscles was produced, which was followed by heart failure.

It is very apparent from the results of the investigations which I have thus briefly summarized, that the *Cactaceae* is a group of plants worthy the attention of the botanist, the chemist, the pharmacologist, the physician, and the toxicologist, as well as the attention of the entire mass of nature-loving human-

ity. It is to be hoped that American scientists will not leave the task of exploring this promising field entirely to workers beyond the sea, considering our proximity to much of the necessary material.

It is the purpose of the present article to bring the subject to the attention of American investigators and to briefly outline the work that has been done in the laboratory of the U. S. Department of Agriculture. "Mescal buttons," the dried, commercial form of *Anhalonium Lewinii*, have served as the starting point for all our investigations. Fig. 1 shows the appearance of the "buttons" when viewed upon the top, upon the edge, and upon the under side.

Figs. 2, 3, 4, and 5, show the appearance of living specimens of *Anhalonium Lewinii*, *A. Williamsii*, *A. fissuratum*, and *A. prismaticum*, respectively, the illustrations being prepared from photographs made by the author from plants growing in the National Botanical Gardens.

An alkaloid corresponding in its properties to Lewin's anhalonin has been prepared in a considerable amount and in a high state of purity. Fig. 6 shows the appearance of the bottom of a crystallizing dish in which the hydrochlorate was crystallized from alcohol by spontaneous evaporation over sulphuric acid in a vacuum.

A second and, very recently, a third alkaloid have been separated from the drug. All three of these alkaloidal preparations have been subjected to physiological tests by Drs. Prentiss and Morgan, and the results of their investigations will soon be published in the *Medical Record*. They have recently published two articles upon the physiological action and therapeutic value of the crude drug in the *Therapeutic Gazette*.<sup>1</sup> As for the third alkaloid separated, let it suffice to say for the present that it has been found to be much stronger than any alkaloid hitherto separated from any member of the genus *Anhalonium*, as 0.02—0.025 gram of its hydrochlorate per kilo or body weight is fatal to rabbits, and 0.03 gram per kilo of body weight suffices to kill a full grown guinea-pig. The hydrochlorate of this alkaloid crystallizes in nodular groups of radiating needles. Fig. 7 was made

<sup>1</sup> Sept., 1895, and Jan., 1896.



from a photograph of crystals obtained by the spontaneous evaporation of a solution of the alkaloidal salt in ninety per cent. alcohol.

An examination of the resinous constituents of the plant is in progress, as well as a study of those of its constituents that are of interest to the vegetable physiologist rather than to the therapist.

A more extended report of this work is reserved for a future paper. Before closing this preliminary announcement, however, I wish to express my indebtedness to Dr. Wiley for much greatly appreciated assistance in the work, and to Dr. Brown for the aid that he very kindly rendered me in the preparation of the photographs used for the illustration of the article. I also desire to express my appreciation of the patience with which both Dr. Wiley and the gentlemen of the Bureau of Ethnology have awaited the progress of this work, which has been largely limited to spare moments not required by other duties.

WASHINGTON, D. C., May 11, 1896.

## THE SULPHURIC ACID PROCESS OF REFINING LIXIVIATION SULPHIDES.<sup>1</sup>

By FREDERIC P. DEWEY.

Received May 21, 1896.

THE time is fast approaching when more chemistry must be used in the extraction of the precious metals in the United States. The chief objections to chemical methods are the technical skill required in the management, the higher grade of labor necessary and the time required to turn out product, thus locking up large amounts of capital; but these difficulties are becoming less applicable all the time. Then too, the wonderful success attained in this country in extracting the precious metals by smelting with lead has retarded the application of chemical methods.

The chemical process of extracting silver by lixiviating, or leaching its ores with solution of hyposulphite of sodium, was introduced by von Paterna in 1858, and has been variously improved, notably by the substitution of the calcium salt for

<sup>1</sup> Read before the Washington Section of the American Chemical Society, March 12, 1896.

the sodium salt. This process, however, had some serious disadvantages, the two most important being the necessity for a high degree of chlorination and the recovery of the precious metals in the form of sulphides.

In order to get a satisfactory extraction it was necessary to chlorinate thoroughly, and this was not always possible, especially in the presence of lime. Mr. E. H. Russell discovered, however, that the addition of a copper salt to the hyposulphite of sodium solution, resulting in the formation of a cuprous sodium hyposulphite, largely increased the solvent power of the solution for the ordinary silver minerals in ores, so that it was not necessary to roast with salt so carefully or so thoroughly; or, with equal care in roasting Russell's "Extra Solution," as it is called, will take out more silver than a plain hyposulphite solution. In other words, the use of the double hyposulphite increased the extraction of silver by the leaching process.

The Russell process can be applied to some ores without roasting, but in general the ores are roasted with salt. They are then charged into large vats and leached with water to extract soluble salts; they are then treated with a succession of hyposulphite solutions of varying compositions and strengths, according to the character of the ore, and are finally washed with water to displace the hyposulphite solution. The tailings are then run to waste. The various solutions carrying the precious metals are gathered up in large vats and precipitated with sodium sulphide. This produces a precipitate of sulphides of gold, silver, copper and a little lead. Most of the lead of the solutions is generally precipitated by a previous treatment with sodium carbonate.

The Russell process has also been applied with marked success to the tailings of other processes, such as amalgamation and the old process of lixiviation with plain hyposulphite. Under favorable circumstances, tailings can be lixiviated for \$1.50 to \$2.00 a ton.

The actual extraction of the silver by the Russell process reaches a high percentage of the total silver present in the ore. In one instance a mill treating nearly 23,000 tons a year averaged nearly ninety-four per cent. for the whole year. With

tailings the extraction is not so high, being from fifty to seventy per cent.

Having brought the extraction of the silver from the ore up to a satisfactory figure there remains the question of dealing with the sulphide precipitate. For a long time this was admittedly the weakest point in the leaching process.

After going through all the operations of crushing, roasting, leaching and precipitating, the best we can say is that we have a rich concentrate, which requires further treatment to convert the precious metals contents into saleable forms.

It is true that these concentrates are often very rich and may even carry a higher silver percentage than the bullion produced by many amalgamating mills, or even by amalgamating the same ores, but the silver, as well as the other metals, are chemically combined with sulphur, and they are also in bad physical condition, being dry powders which are very susceptible to loss in handling, while their sampling and assaying present unusual difficulties.

The improvement in leaching, introduced by the Russell process and the success of this process has stimulated the development of processes for refining the sulphides. In the early days several processes of dealing with the sulphides were proposed and some of them tried more or less, but the business finally settled down to sending the sulphides to the smelters for treatment, although this was well known to be troublesome and expensive. In 1891 Mr. C. A. Stetefeldt introduced at the Marsac Mill, Park City, Utah, an unpatented process which was built up out of the general fund of information available. The process consisted in matting the sulphides, grinding, roasting, grinding again and dissolving the copper out in dilute sulphuric acid, then melting the silver and crystallizing the bluestone. It did not yield fine bullion, but the bullion had to be refined as well as parted, besides there was some loss. This process was thoroughly tried at the Marsac Refinery, and then a year's run was made, the net results of which was that it did not prove sufficiently better than sending the sulphides to smelters.

In 1893 the Dewey-Walter Refining Company undertook the refining of the Daly sulphides in the the Marsac Refinery by the

sulphuric acid process, upon which a United States patent has been issued to the writer. Naturally difficulties were encountered in starting a new process and much of 1893 was taken up in getting the process into smooth working order, but in 1894 a run was started in which all the regular sulphides produced by the Marsac Mill in 1894 were refined and thus a complete set of statistics of the operation of the process was obtained.

Broadly speaking the process consists of six main operations:

*First.* Boiling the sulphides with strong sulphuric acid in an iron pot.

*Second.* Dissolving out the sulphates of copper and silver in a lead lined tank, leaving a residue containing the gold and lead of the sulphides and also rich in silver.

*Third.* Precipitating the silver out of the filtered solution by copper plates.

*Fourth.* Sweetening, drying, pressing and melting the cement silver.

*Fifth.* Treatment of the solutions after the removal of the silver to crystallize the sulphate of copper and recover the excess of acid for reuse.

*Sixth.* Treatment of the gold-bearing residues.

The 1894 run of the Marsac Leacher produced 116,519½ pounds of regular sulphides, which were treated by this process. For convenience they were divided into twenty-five lots, mostly from 4,500 to 5,500 pounds in weight. As reported by the assayer of the Daly Mining Company, these lots varied in composition as follows:

#### COMPOSITION, DALY SULPHIDES FOR 1894.

	Silver. Ounces per ton.	Gold. Ounces per ton.	Copper. Per cent.	Lead. Per cent.
Maximum.....	11,127	14.8	32.9	0.2
Minimum .....	7,835	7 6	20.3	0.6
Average .....	9,827.4	11.225	27.17	0.33

The totals were:

Silver .....	572,544.4 ounces.
Gold .....	646.1 "
Copper .....	31,585.3 pounds.
Lead .....	385.6 "

## THE PLANT.

The plant required is simple and all of it is well known. It is easily managed and no especially skilled labor is required. It consists of two ordinary iron pots, such as are used in parting bullion ; a series of twenty-one lead-lined tanks for dissolving, filtering the solutions, precipitating the silver and filtering off and sweetening the cement silver, together with crystallizers to recover the bluestone, and evaporators to concentrate the mother liquors for reuse in the pot ; a dryer and press for the cement silver ; furnace for melting the bullion ; four storage tanks for acid ; and pumps for handling the liquids. The large pot for boiling the sulphides is forty-six inches in diameter and three feet deep. It is hung by its rim on a cast iron plate and is enclosed in brick work over a fire-box. It stands fourteen feet from the floor and is provided with a suitable hood and stack to take off the fumes. The smaller pot is used for boiling the residues. The tanks are arranged in steps to allow the descent of the solutions from one to the other by gravity.

## THE PROCESS.

The process consists in boiling the sulphides in strong sulphuric acid to convert the sulphides into sulphates. The sulphate of silver is soluble in strong sulphuric acid, but the anhydrous sulphate of copper is practicably insoluble. Owing to the large percentage of copper, averaging twenty-seven per cent. in 1894, in the sulphides a large quantity of insoluble sulphate is produced, and this is one of the most serious difficulties of the process. After boiling the charge is removed to the dissolving tank, in which are put wash water and weak solutions. Here the copper sulphate goes into solution along with the silver. The solution is filtered into the precipitating tanks where the silver is precipitated by metallic copper, after which the solutions are concentrated and go to the crystallizers to recover the bluestone. Periodically the cement silver is removed to the filter, sweetened, dried, pressed and melted. The mother liquors are concentrated, crystallized and the recovered acid finally sent back to the pot. The residue in the dissolving tank is taken out, washed somewhat and reboiled in acid to remove as much as possible of the silver that it contains.

## PRACTICAL OBSERVATIONS.

A charge of about 975 pounds is put into the pot in the morning with about 1,000 pounds of 66° acid and thoroughly mixed and the charge heated. At first the reaction is rather violent; sulphur dioxide is copiously evolved and the fumes carry considerable sulphur, which gives them a yellowish color. At this stage a steam jet may be required to increase the draught. After a while the reaction settles down and the normal charge boils quietly until near the end. As soon as the charge gets stiff, more acid, about 100 pounds, is added, until about 3,000 pounds have been added. Toward the end, evaporated acid is used. As the boiling goes forward anhydrous sulphate of copper is formed in large quantities which separate, forming granular masses. This necessitates frequent stirring of the charge and this in turn is hard on the pots. A net-work of cracks develops and finally the acid finds its way through, when the pot must be replaced. In the 1894 run nine pots were used, two of which were short-lived. Better results have been obtained since.

The progress of the operation can be watched by taking out a small sample of the charge, treating with water and adding hydrochloric acid to the solution; but this is not necessary after getting familiar with the process, since the color changes from black to brown or dark gray. About ninety per cent. of the total acid used is added before the charge begins to show soluble silver salts. Then the charge foams violently and must be constantly stirred while the fire must be lowered. In about an hour the foaming is over and the charge is finished. This usually occurs in the afternoon of the day after starting. On the second morning the charge is warmed up, generally with the addition of some acid and, as it is rather thick, it is ladled out into a trough which delivers it to the dissolving tank. The pot is then started on a new charge.

The dissolving tank is filled with cold water within six or eight inches and tightly covered, since the introduction of the charge generates much heat. After the charge is in, the cover is raised and the solution stirred with a paddle and boiled with steam, after which it is settled and drawn into the filters. The

first tankful of solution contains most of the copper. It is run into a small precipitating tank and kept separate from the rest of the solution. The charge now resembles thick white mud and is washed eight or ten times with weak acid solutions to remove the silver, after which the residue is thrown into a filter. This residue varies very much, running from 5,000 to 19,000 ounces silver per ton and fifty to 100 ounces gold, the balance being mainly sulphate of lead.

The filters are three to four inches of clean quartz sand on a foundation of lead plates, cocoa matting and asbestos cloth, resting on lead strips, giving a space below. It is impracticable to settle all the very fine residue in the dissolving tank, so some of it passes over into the filters and chokes them up. In about two weeks the filters must be washed by a stream of water from below and the muddy water pumped off the top.

The solution has a reducing action and immediately a separation of metallic silver begins in the dissolving tank, often with the formation of beautiful growths upon the surface of the liquid, and this reaction continues in the filters. By this reaction metallic silver is found in the first residue and some 10,000 ounces may accumulate in the filters during a year's run.

From the filters the solution goes to the precipitating tanks, where the silver is precipitated by copper, cathode plates from an electrolytic refinery being used. The first or copper solutions require a long time to precipitate, sometimes eighteen hours, but ordinary solution is precipitated in four to five hours. During precipitation the solution is stirred by air and heated by steam. When the precipitating tank is cold and the hot solution of silver sulphate runs in, there may be a separation of silver sulphate which may go into the solution again as the solution is heated up, but some of it may also remain with the cement silver and be removed in washing the silver, in which case the wash water must be treated with copper.

When about 20,000 ounces of cement silver have accumulated in the precipitating tanks, it is removed to the sweetening tank and washed with hot water and then with acidulated hot water until the ammonia test shows no copper, which takes about fif-

teen hours. The wash water runs through a guard tank containing scrap iron and then to waste.

The sweetened silver is put into sheet iron pans and dried about twenty-four hours in a steam dryer, pressed into cakes, dried again and melted. In 1894 the melting was done in crucibles holding about 2,400 ounces, or two bars, and about a pound and a half each of borax and niter were used to a crucible. The melted silver was poured into heated and greased light cast steel moulds. After pouring a little sugar was thrown on the liquid silver and the mould covered by a tight fitting cast iron cover. This gives a very smooth surface to the bar. When cool the bars are hammered up and marked. The average fineness for 1894 was 999.4 silver with no gold, 446 bars were shipped, of which 401 were 999.5 fine and forty-five were 999.0 fine.

The bluestone solutions are concentrated to about 35° to 37° B, and run into ordinary crystallizers provided with lead strips and allowed to stand two days or more, when it is pumped back to the evaporators and run up to 42° B. It goes back to the crystallizers, and a crop of crystals containing iron and but little bluestone is obtained. The solution goes back to the evaporator. The crystallizers are filled with cold water, which dissolves most of the iron and only a little of the copper. This solution goes through the guard tank to waste. These bluestone crystals are very small, but answer well in the leacher in preparing extra solution. The mother liquid is brought up to 50°-52° B. and then allowed to stand in a crystallizer several days to separate iron. It is then pumped to storage tanks for use in the pot. While concentrating, considerable iron separates in the evaporators. Periodically this is washed out and the solution run to waste through the guard tank.

After boiling five charges of sulphides, about 750 pounds of wet residue are obtained. This is put into the pot and boiled with a little more than its own weight of acid, after which it is washed and the final residue dried. This residue is very complex in composition, although it is mainly sulphates of silver and lead. There appears to be some acid sulphate, for the sulphuric acid present is far more than sufficient to form normal sulphates, and



yet the sample is so dry that the excess of acid cannot all be free. It contains the gold of the sulphides. During 1894 this residue was shipped away to the smelters for treatment, but at the present time it is being melted on a hearth.

#### SUPPLIES.

Sulphuric acid is received at the refinery in iron tank cars holding 40,000 to 50,000 pounds. It is stored in two lead-lined wooden tanks and is elevated by a mountejus to two iron receivers above the level of the pots from which it is drawn to feed the pots. In the 1894 run 389,439 pounds were used, being an average of 3.34 pounds per pound of sulphides treated, or 0.68 pound per ounce of silver. Copper to precipitate the silver is used in the form of cathode plates, and 16,832.5 pounds were used, one pound of copper precipitating 2.27 pounds of silver, or 33.1 troy ounces. The ordinary local coal is used and 159,000 pounds were used in the 1894 run. The regular labor required was a superintendent and two men, with an extra man to assist the superintendent in melting bullion. Occasionally some extra labor was required, particularly in shipping residue and making the annual clean-up. Mechanics were also required for special work occasionally, but the lead burning was done by one of the regular men.

#### RETURNS.

It is a well known fact that, in assaying, some of the precious metals pass into the slag, and some are absorbed by the cupel, causing a loss in the determination. In the case of ordinary ores, this quantity per ton is generally small, although the percentage of the total silver is large. In the case of rich materials, however, the percentage is low and the actual quantity per ton becomes considerable, and when the rich material carries copper the loss of silver per ton becomes quite respectable. In our business transactions, the sulphides are always settled for upon an assay corrected for slag and cupel absorption, which shows from 100 to 200 or even more ounces per ton more than ordinary uncorrected assay shows. Even on the corrected assay the actual amount of silver returned by the refinery on the year's work was 2,078.81 ounces more than the assays called for, show-

ing very plainly that even the corrected assays do not show all the silver really present. This silver was divided as follows :

116,519.5 pounds sulphides contained 572,544.45 fine ounces of silver.

PRODUCT RETURNED.

	Fine ounces silver.	Per cent. total silver.
Fine bullion, free from gold.....	551,329.89	96.29
Residue.....	15,773.41	2.79
Cleanings.....	5,328.87	0.93
On hand .....	2,191.09	0.38
<hr/>		
Total .....	574,623.26	100.36
Plus clean-up .....	2,078.81	0.36

All weights of sulphides and products, excepting one covering less than 200 ounces, and all the assays are the originals made by the Daly Mining Company.

It is regarded as an extraordinary showing for a chemical process on the large scale to recover more than the best assay possible calls for.

As to the recovery of gold, I cannot see any reason why it should not equal the silver recovery, but the figures upon the point are not satisfactory. The actual return of gold for the year was 606.9 ounces. The original assay of the Daly Mining Company called for 654.8 ounces, but their re-assay on some of the samples reduced this to 646.1. This left an apparent shortage in the returns of 39.2 ounces. The same samples were assayed by Mr. Charles Earl under my directions, and while the silver result showed a satisfactory agreement with the Daly assays, yet his gold determinations called for only 602.9 ounces, showing a plus clean-up on the year's work of four ounces. After the close of the year's business a general sample was prepared by taking proportionate weights of each of the check samples of the twenty-five lots, and the Daly Co.'s assay of this sample called for 605.9 ounces, and showed a plus clean-up of one ounce. Mr. Earl is no longer with me, so I cannot add his figures on this sample. There are especial difficulties in determining such small quantities of gold in the presence of so much silver.

The conditions of the process are such that I do not see how we could gain so much on the silver and lose on the gold, so that I am satisfied that the process practically recovers all the gold that goes into the operations, although the assays may not always show this.

The bluestone produced amounts to 175,809 pounds, or 3.63 pounds per pound of copper, including the copper in the sulphides and the copper used to precipitate the silver. About 125,000 pounds of bluestone were used by the leacher in preparing extra solution, leaving 50,000 pounds to be sold to outside parties. No particular care is taken to prepare fine large crystals of bluestone, and it is not necessary to purify the solutions from iron except as above described. Most of the bluestone produced goes to the leacher and the size of the crystals is of no moment whatever, while the small amount of iron present does no harm. The best grade showed 0.34 per cent. of protoxide of iron, the medium 0.69 per cent., and the worst, of which only a small quantity was produced, 3.89 per cent.

THE FOLLOWING TABLE SUMMERIZES THE STATISTICS FOR THE YEAR BY THE DEWEY-WALTER PROCESS OF BOILING RUSSELL SULPHIDES IN STRONG SULPHURIC ACID.

First charge of 1894 sulphides to pot, February 20, 1894.

" " " 1895 " " " February 27, 1895.

Sulphides treated, 116,519.5 pounds.

" contained silver by corrected assay, 572,544.45 ounces.

" " copper, 31,585.3 pounds.

" " lead, 385.6 pounds.

" " silver average ounces per ton, 9,827.44.

" " copper average per cent., 27.1 per cent.

" " lead average per cent., 0.33 per cent.

Acid used, 389,439 pounds.

" " per pound sulphides, 3.34 pounds.

" " per ounce silver, 0.68 pound.

Coal, 159,000 pounds.

Copper used to precipitate silver, 16,832.5 pounds.

Total copper, 48,417.8 pounds.

One pound copper precipitated silver, 2.27 pounds.

Bluestone produced, 175,809 pounds.

" " per pound copper, 3.63 pounds.

Regular labor, superintendent and two men.

Extra labor, one man at bullion melting to assist superintendent, laborers for clean-up and shipping residue, etc., mechanics for special work occasionally.

136,519.5 pounds sulphides contained 572,544.45 fine ounces of silver.

PRODUCT RETURNED.

	Fine ounces silver.	Per cent. total silver.
Fine bullion, free from gold.....	551,329.89	96.29
Residue.....	15,773.41	2.76
Cleanings.....	5,328.87	0.93
On hand.....	2,191.09	0.38
<hr/>		
Total.....	574,623.26	100.36
Plus clean-up.....	2,078.81	0.36

All weights of sulphides and products, excepting one covering less than 200 ounces, and all the assays are the originals made by the Daly Mining Company.

The advantages of this process are the phenomenal percentage of silver recovered, and that it is an entirely liquid one from beginning to end, so that there is no loss from handling dry products. There is no roasting to cause loss. A large percentage of the silver is recovered as very fine bars, ready to enter the market. It is so simple and so easily carried out, and the plant is so small and inexpensive that it can be installed at individual leaching works.

Finally, the cost of operating is small; in fact, the value of the bluestone recovered returns a large proportion of the operating expenses.

## NOTES ON THE ELECTROLYTIC DETERMINATION OF IRON, NICKEL AND ZINC.

BY H. H. NICHOLSON AND S. AVERY.

Received May 15, 1896.

THE experimental part of this work was undertaken in the spring of 1892. During the progress of the work various articles on the electrolytic department of these metals have been published. Some of these investigations are closely related to those carried out by us. As, however, they differ in some important particulars and as some observations have been made which, so far as we are aware, have not as yet been reported, it

seemed well to present the results obtained although some parts of the work are still incomplete.

In the method of manipulation, free use was made of the text-books of Classen and of Smith. A number of cells of the Grove-Tyndall form furnished the current. The current was controlled by means of a rheostat-box. The amperage was determined by means of a "Weston" volt-meter. The metals were deposited in platinum dishes of 300 cc. capacity.

In no case was any attempt made to separate metals by careful regulation of the voltage as the practical utility of such methods may be doubted till the literature of the subject is more copious.

#### I. THE ELECTROLYTIC DEPARTMENT OF IRON.

The method of Classen and V. Reiss<sup>1</sup> for the determination of the metals in their double oxalate solutions, a method which gives such admirable results in most determinations, cannot be applied with the same degree of convenience to iron, as a strong, current and a hot solution are necessary.

Smith and Muir<sup>2</sup> found that iron is very readily precipitated from ammonium tartrate solutions containing free ammonia. They found, however, that under such circumstances the iron contains carbon. Still tartrate solutions seemed to offer possibilities for quantitative determinations sufficient to warrant a fuller investigation of the subject.

Six grams of tartaric acid was dissolved in water and added to a solution of ferrous sulphate. The solution was then diluted to 150 cc. and rendered strongly alkaline with ammonia. The solution was then placed in a platinum dish, submitted to the action of a current of 0.115 ampere and four volts for six hours.

Taken 0.0477 gram iron. Weight found 0.0476 gram iron.

After weighing, the precipitate was dissolved in dilute sulphuric acid. A trace of the odor of hydrocarbons was present. The solution was then oxidized; precipitated with ammonia and determined in the usual gravimetric way. The weight of the iron oxide corresponded to 0.0465 gram of iron. The carbon present evidently compensated for the weight of the unprecipitated iron.

<sup>1</sup> *Ber. d. chem. Ges.*, 14, 1622.

<sup>2</sup> *J. Anal. Chem.*, 5, 488.

The following determinations were made in a similar manner :

No.	Current amperes.	Time. Hours.	Solution.	Iron taken. Gram.	Weight found. Gram.	Carbon by difference. Gram.
1	0.185	4	Strongly alkaline.	0.0620	0.0418	....
2	0.115	14	Strongly alkaline.	0.0476	0.0487	0.0011
3	0.115	6	Slightly alkaline.	0.0291	0.0294	0.0003
4	0.5	5	Strongly alkaline.	0.0476	0.0492	0.0018
5	0.5	5	Strongly alkaline.	0.0351	0.0364	0.0013

These figures show that strong currents and free ammonia are favorable to the precipitation of carbon. Hence attention was turned to the electrolysis of iron in neutral ammonium tartrate solutions.

To twenty-five cc. of an iron sulphate solution, sodium hydroxide was added till the greater part of the iron was precipitated. A dilute solution of tartaric acid was now added till the greater part of the precipitate was dissolved ; five grams of ammonium tartrate were added and the whole diluted to 150 cc. The solution made up in this way was found to be exactly neutral to litmus. It was necessary to employ a stronger current than when free ammonia was present. The following determinations were made :

No.	Current. Amperes.	Time. Hours.	Iron taken. Grams.	Weight found. Grams.	Iron calculated from $\text{Fe}_2\text{O}_3$ . Grams.
1	0.4	6	0.0630	0.0634	....
2	0.4	6	0.0630	0.0635	....
3	0.5	4½	0.0630	0.0626	0.0620

In all cases carbon was detected in the precipitated iron.

Attention was next given to the determinations of iron in sodium tartrate solutions. In some cases free sodium hydroxide was present. The sodium salt conducts the current much better than the ammonium salt. The precipitation of iron proceeds satisfactorily for a time. After a little black spots appear. When a strong current is employed a white precipitate of ferrous carbonate forms on the deposited metal. Currents of two to four volts and of 0.05 to 0.1 amperes were employed to effect the separation of the iron from the solution. Towards the end of the precipitation carbon deposits rapidly. Vortmann,<sup>1</sup> by using

<sup>1</sup> *Chem. Centrbl.*, 1893, 1070.

currents of low voltage and precipitating the iron in fractions on weighed electrodes, seems to have avoided some of the unfavorable conditions above described. However the general deportment of iron in sodium tartrate solutions was so unpromising that the investigation was not carried further in this direction.

The question now presented itself: "Is the precipitation of carbon with iron peculiar to tartrates or may we expect it when other organic compounds are present?"

To answer this question a number of qualitative tests were made by adding to the iron solution before passing the current, solutions of sugar, alcohol, glycerol or of salts of formic, acetic, lactic, citric, succinic or benzoic acids. The currents employed were of the lowest voltage and amperage sufficient to give a deposit of several milligrams in the course of an hour. As ammonium oxalate gives no precipitate of carbon under any circumstances, so far as we are aware, this reagent was used to hold the iron in solution when necessary. The iron was used in the form of ferrous sulphate.

When formates were present in the absence of other organic compounds, no trace of carbon could be detected in the precipitated iron. In all other cases the precipitated iron contained carbon. In the case of citric acid a quantitative determination was made.

A solution of ferrous sulphate containing five grams of citric acid in the form of sodium and potassium salts with a little free acid was submitted for fourteen hours to a current of 0.2 ampere.

Taken 0.0726 gram iron. Weight found 0.0740 gram iron.

The absence of carbon in the case of oxalates and formates is explained by the fact that these compounds break up under the influence of the current giving off all carbon in the form of its highest oxidation product, *i. e.*, carbon dioxide.

In all cases the amount of carbon deposited was increased by the employment of stronger currents, but in no case was it possible to obtain a precipitate free from carbon, except in the case of formates and oxalates, when organic matter was present.

#### DETERMINATION OF IRON IN SOLUTIONS CONTAINING AMMONIUM OXALATE AND SODIUM BORATE.

We found that a slight modification of Classen's method

greatly facilitated the precipitation of iron. The following gave satisfactory results:

Twenty-five cc. of a solution of ferrous sulphate were taken, five grams of ammonium oxalate were added and brought into solution by the aid of gentle heat. Five cc. of a saturated solution of borax were now added and the entire solution diluted to 150 cc. A current of 0.02 ampere was allowed to act on the cold solution for sixteen hours. Towards the end of the operation the anode became covered with a slight brown coating. A slight brown deposit also appeared on the dish above the iron deposit. The following method was used to dissolve these deposits. Water was added until the surface of the liquid was raised above the brown deposit in the dish. The positive electrode was then brought in contact for a moment with the side of the dish thus short-circuiting the battery and generating considerable heat in the electrodes. This had the effect of liberating and dissolving the brown deposit. The current was allowed to act for half an hour longer when the dish was removed from the circuit, washed, dried and weighed.

The precipitate was perfectly adherent and showed no tendency to oxidize when washed with alcohol and ether. The following is a tabular statement of the results obtained :

No.	Ammonium oxalate. Grams.	Saturated borax solution. cc.	Current. Ampere.	Time. Hours.	Iron taken. Gram.	Iron found. Gram.
1	5	5	0.02	16	0.0938	0.0933
2	5	10	0.02	17	0.0938	0.0935
3	6	10	0.06	4	0.0938	0.0938
4	5	5	0.072	2	0.0938	0.0939
5	6	5	0.125	2	0.0938	0.0938

It will be seen from the above that the presence of borax facilitates the precipitation of iron in ammonium oxalate solutions. The cause of the appearance of the slight brown deposit and the extent to which it might cause an error in results will be investigated later.

## II. THE DETERMINATION OF NICKEL.

The determination of nickel presented no difficulties. The greater part of the experiments with iron were performed in an



analogous way with nickel: in no case was carbon deposited with the nickel. When iron and nickel are deposited together as an alloy in the presence of organic compounds the nickel does not prevent the contamination of the precipitate with carbon.

### III. DETERMINATION OF ZINC.

Nearly all the published methods for the electrolytic determination of zinc give fairly satisfactory results. The tendency of the metal to be deposited in a spongy condition and the liability to oxidation are the principal difficulties usually encountered.

The tendency to oxidation may be prevented by the presence of formic acid in the solution, which by the liberation of hydrogen with the metal exercises a reducing action.

By the electrolysis of zinc formate in the presence of formic acid Warwick<sup>1</sup> did not succeed in obtaining a complete deposit. The deposit is greatly influenced by the presence of sodium formate in the solution.

To a solution of zinc sulphate three cc. of formic acid were added and the solution partially neutralized with one gram of sodium carbonate. The entire solution was diluted to 150 cc. and placed in a current of 0.02 ampere for three hours.

Taken 0.0611 gram zinc. Found 0.0603 gram zinc.

In a similar manner the following determinations were made:

No.	Formic acid. cc.	Sodium carbonate. Gram.	Current. Ampere.	Time. Hours.	Weight taken.	Weight found.
1	4	1.5	0.125	3	0.0611	0.0612
2	5	1.0	1.000	3	0.0611	0.0611
3	5	1.0	0.050	3	0.0611	0.0611

The deposit adhered well, was compact and evenly distributed on the surface of the dish, the color was light gray, in some cases almost metallic in luster. As will be seen from the figures, a considerable variation in the strength of the current is allowable. This method is not allowable in the presence of the metals of the hydrogen sulphide group, as well as in the presence of iron, nickel and cobalt.

CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA.

<sup>1</sup> *Ztschr. anorg. Chem.*, 1, 291.

**CORRESPONDENCE.**

UNITED STATES DEPARTMENT OF AGRICULTURE,  
DIVISION OF CHEMISTRY,

WASHINGTON, D. C., June 5, 1896.

*Editor Journal of the American Chemical Society, Easton, Pa. :*

DEAR SIR.—I am informed by the Chairman of the Committee of Arrangements of the Second International Congress of Applied Chemistry, that the meetings of the Congress will begin in Paris on the 27th of July, at the Sorbonne, at 10 o'clock A. M. The meetings of the Congress and of the Sections will be continued until the 7th of August.

Chemists intending to present papers should send the titles, without delay, together with the length of time required, to Monsieur F. Dupont, 156 Boulevard de Magenta, Paris, France. Those who intend to be present in person should also inform Monsieur Dupont of that fact.

Respectfully,

H. W. WILEY,

Chairman of American Committee.

**BOOKS RECEIVED.**

Bulletin No. 43. Composition and Digestibility of Corn Ensilage, Cow Pea Ensilage, Soja Bean Ensilage, and Corn Fodder. University of Illinois, Agricultural Experiment Station, Urbana, Ill. April, 1896. 28 pp.

Special Bulletin. Commercial Fertilizers. Purdue University, Lafayette, Ind. May, 1896. 8 pp.

Bulletin No. 17. Hay Substitutes. Storrs Agricultural Experiment Station, Storrs, Conn. June, 1896. 8 pp.

Bulletin No. 38. (1) General Discussion on Commercial Fertilizers. (2) Analyses of Fertilizing Materials Sent On for Examination. (3) Observations Regarding the Composition of Paris Green. (4) Observations Concerning the Action of Muriate of Potash on the Lime Constituents of the Soil. Hatch Experiment Station of Massachusetts Agricultural College, Amherst, Mass. March, 1896. 16 pp.

Bulletin No. 39. Economic Feeding of Milch Cows. Hatch Experiment Station of Massachusetts Agricultural College, Amherst, Mass. April, 1896. 23 pp.

Bulletin No. 63. Tobacco. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. May, 1896. 20 pp.

Yearbook of the United States Department of Agriculture, 1895. Washington: Government Printing Office. 1896. 656 pp.

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